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Global Distribution of Selected Halocarbons, Hydrocarbons, SF6, and N2O

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GLOBAL DISTRIBUTION OF SELECTED HALOCARBONS, HYDROCARBONS, SF_6, AND N_2O

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ABSTRACT

Northern and Southern hemispheric distributions of halogenated species, hydrocarbons, SF_6 and N_2O are presented. The atmospheric growth rates of selected halocarbons and N_2O are characterized. The fluorocarbon 11 and 12 global burden and hemispheric distribution is consistent with the view that no significant sinks in the troposphere exist. The north-south gradients of fluorocarbon 11, 12, 113, 114, CCl_4, and SF_6 suggest rapid global mixing with an interhemispheric exchange rate of about one year. Within each hemisphere, these species are well mixed. N_2O shows the least variations around the globe. The global distribution of CH_3CCl_3 is found to be complex and suggests higher HO levels in the southern hemisphere and around the equator, when compared to the northern hemispheric HO levels. The global distribution of CH_3Cl is almost uniform and a significant natural source has been identified in the ocean. It is also shown that large anthropogenic primary or secondary sources of CH_3Cl and CCl_4 exist. Species such as $CHCl_3$, CH_2Cl_2, C_2HCl_3, and C_2Cl_4 show very large north-south gradients. The atmospheric growth of fluorocarbons 11, 12, CH_3CCl_3, and CCl_4 appear to be consistent with the emissions of these constituents.

It is found that the world oceans may provide a sink for CCl_4 which is about half as effective as the stratospheric sink. For CH_3Cl a significant source appears to exist in the ocean. Fluorocarbon 11 and 12 concentration in Pacific seawater show some evidence of supersaturation. The lowest levels measured indicate that the surface ocean waters are in essential equilibrium with the atmospheric concentrations of F12 and F11.

The Pacific Ocean (45°N-40°S) is found to be a significant source of N_2O despite the high oxygen content in the South Pacific. The N_2O variabilities in the troposphere are small and an N_2O residence time of as much as 70 years is possible. No increase of N_2O in the atmosphere was observed over the last 27 months. Our data imply that continued use of fertilizer is unlikely to pose a threat to the stratospheric ozone.

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INTRODUCTION

This report presents the Phase II results obtained during the second year of a continuing study dealing with the atmospheric fate of halogenated compounds. We attempted to characterize the global abundance of important atmospheric trace constituents likely to affect the stratospheric ozone. The abundance of these trace constituents was determined in the atmosphere and in the ocean in both hemispheres. These data are essential for obtaining important information on the lifetimes of trace constituents, interhemispheric exchange rates, and the strength of atmospheric and oceanic sinks. This information is also necessary for calculation of stratospheric ozone depletion.

OBJECTIVES

The objectives of Phase II were:

- To determine the atmospheric distribution and abundance of selected halocarbons, hydrocarbons, SF_6, and N_2O in the northern and southern hemispheres.
- To determine the ability of the oceans to act as a source or a sink of the important trace constituents.

The objectives of Phase II were designed to complement the following overall objectives of this project:

- To determine the distribution, atmospheric loading, sources, and sinks of halogenated compounds, selected photochemical pollutants, and natural trace constituents with possible stratospheric impact.
- To use halocarbons to improve understanding of complex regional and global atmospheric transport phenomena having a bearing on pollution control strategies.
- To use halocarbons as reactive tracers to improve understanding of natural tropospheric chemistry.

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SUMMARY OF RESULTS

Global atmospheric budgets and distributions of a large number of halogenated species, hydrocarbons, SF_6, and N_2O were determined between 63° N and 90°S at different longitudes. Background air samples were analyzed both in-situ and by collecting pressurized air samples in specially constructed vessels. Pacific seawater samples from 46°N to 40°S were also analyzed; the samples were obtained from depths of 0 to 300 m at 50-m intervals.

Table 1 shows the background concentrations of important trace constituents in the northern hemisphere (N.H.) and the southern hemisphere (S.H.). When a significant gradient exists within one hemisphere, the average concentration is defined as the concentration that, when mixed uniformly within the hemisphere, represents the total burden of the species in that hemisphere.

The north-south average concentration difference for inert fluorocarbons is about 5 to 10%, and each of the hemispheres is reasonably well mixed. We did not observe any evidence of important longitudinal variations within each hemisphere. For N_2O, CCl_4, CH_3Cl, and CH_4 the north-south concentration differences are even smaller and vary between 0 and 4%. Other species such as CH_3CCl_3 and C_2H_6 show a more complex latitudinal distribution. The latitudinal distribution of CH_3CCl_3, for example, is best described by the following cubic function:

$$C_{CH_3CCl_3} \text{ (ppt)} = 89.710 + 0.818\ L + 7.584 \times 10^{-4}\ L^2 - 7.894 \times 10^{-5}\ L^3 \quad (1)$$

where ppt is parts per trillion, L is the latitude, varying from 0 to +90° for the N.H. and 0 to -90° for the S.H. Indeed, CH_3CCl_3 distribution shows a rapid drop from 20°N to 20°S latitude. The analysis of CH_3CCl_3 distribution supports our earlier findings of low global HO abundance, and higher HO levels near the equator and in the S.H. than in the N.H. We suggest that this gradient is caused by atmospheric carbon monoxide (CO), which is an effective sink for HO.

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Table 1

AVERAGE BACKGROUND CONCENTRATIONS OF IMPORTANT TRACE CONSTITUENTS

Compound	Concentration* (ppt)†		
	N.H. Average	S.H. Average	Global Average
N_2O	311×10^3	311×10^3	311×10^3
CCl_2F_2 (F12)	230	210	220
CCl_3F (F11)	133	119	126
CCl_2FCClF_2 (F113)	19	18	18
$CClF_2CClF_2$ (F114)	12	10	11
$CHCl_2F$ (F21)	5	4	4
SF_6	0.31	0.27	0.29
CCl_4	122	119	120
CH_3CCl_3	113	75	94
CH_3Cl	611	615	613
CH_3I	2	2	2
$CHCl_3$	14	≤ 3	8
CH_2Cl_2	44	20	32
C_2HCl_3	16	<3	8
C_2Cl_4	40	12	26
CH_4	1430×10^3	1390×10^3	1410×10^3
C_2H_6	1060	524	792
C_2H_2	<200	<200	<200

*For those species where significant variations within each hemisphere were observed, the average concentration within each hemisphere is the concentration that, when uniformly mixed in the hemisphere, represents the total burden of the species in that hemisphere.

†ppt = 10^{-12} v/v.

While most trace halospecies seem to be of uniquely anthropogenic origin, dominant natural sources of CH_3Cl and CH_3I are indicated. Contrary to the currently held view, our measurements in urban areas suggest that significant anthropogenic sources of CH_3Cl and CCl_4 must exist.

The N.H. and S.H. distributions of inert fluorocarbons and SF_6 suggest rapid global mixing, with an interhemispheric exchange rate of about one year. The budgets of F11 and F12, as measured by us, are compatible with an overall residence time of 45 years for F11 and about 60 years for F12. This is consistent with our earlier assertion that there are no significant tropospheric sinks (Singh, 1977a). For other species such as $CHCl_3$, CH_2Cl_2, C_2HCl_3, and C_2Cl_4 a significant north-south gradient is evident, and is indicative of rapid tropospheric removal processes.

Table 2 shows the average growth rates of N_2O, CCl_2F_2, CCl_3F, CCl_4, and CH_3CCl_3 at around 40°N. The average growth rates of halocarbons agree with projected emissions. It appears that the background levels of N_2O are unchanged.

The N_2O distribution in the globe is both uniform and nonvariable. The atmospheric variability of N_2O (σ = 0.7%) suggest a residence time of 20 to 60 years.

Table 2

AVERAGE ATMOSPHERIC GROWTH RATES OF IMPORTANT SPECIES FROM NOVEMBER 1975 TO DECEMBER 1977

Compound	Average Growth Rate*	
N_2O	0.9 ppb/yr†	0.3 (≈0) %/yr
CCl_2F_2 (F12)	18.5 ppt/yr	10%/yr
CCl_3F (F11)	12.9 ppt/yr	12%/yr
CCl_4	2.3 ppt/yr	2%/yr
CH_3CCl_3	15.5 ppt/yr	17%/yr

*Based on data collected between 35°N - 40°N.

†More precise comparisons indicate an average change of -0.1% per year (see Table 6).

The Pacific Ocean is significantly supersaturated with N_2O. Average surface saturation of 133% and a maximum saturation of 190% were measured between 46°N and 39°S. The N_2O concentration below the mixed layer varied from 1 to 7 times the surface concentration, with a maximum near the equatorial region. The supersaturation below the mixed layers was marginal at midsouthern latitudes. An oxygen content of 3 to 4 ml/l is not too high for significant N_2O production. This observation suggests that either nitrification processes that are efficient in the presence of relatively high O_2 content play a more important role in N_2O production than hitherto believed, or denitrification processes are poorly understood and can proceed under conditions significantly different from anoxic.

A global N_2O oceanic flux of 32.4 million tons per year has been calculated. When one includes fresh-water sources, we estimate an N_2O source of 35 million tons per year. This corresponds to a turnover rate of 67 years, which agrees with the upper limit of 60 years estimated from atmospheric variability data. Since the stratospheric sink has been estimated to result in a turnover time of 120 years, a unknown sink with a N_2O turnover time of 150 years can be inferred. Soil may be such a sink. As long as the ocean is the major source of N_2O, any effect on N_2O abundance from increased use of fertilizer is likely to be insignificant. The atmospheric abundance of N_2O in December 1977 was within 0.2% of the September 1975 abundance.

The average Pacific surface water concentrations (ng/l) of CCl_2F_2, CCl_3F, CCl_4, CH_3Cl, and $CHCl_3$ were found to be 0.28, 0.13, 0.40, 26.8, and <0.05, respectively. Both CCl_2F_2 and CCl_3F surface water concentration indicated some supersaturation. The lowest measured concentrations of CCl_2F_2 and CCl_3F in seawater were essentially in equilibrium with their atmospheric concentrations. In the case of CCl_4, world oceans were found to be a sink about half as effective as the stratospheric sink. From the limited data, it would seem that the world oceans could provide a CH_3Cl source of about 5 million tons per year. This source can provide a turnover rate for atmospheric CH_3Cl of about 2 years.

EXPERIMENTAL PLAN AND SAMPLING AND ANALYSIS PROTOCOL

The Phase II study consisted of four experiments. In each case samples were collected from the northern and the southern hemispheres and analyzed either immediately or later. The highest latitude in the northern hemisphere from which samples were collected and analyzed was about 64°N. In the southern hemisphere samples were collected up to 42°S, and additional samples were obtained from 90°S to obtain maximum coverage. Sampling always began in the northern hemisphere and continued into the southern hemisphere. Briefly the four experiments were as follows:

AIR SAMPLING AND ANALYSIS

Experiment 1

Pressurized air samples were collected between 64°N and 20°S in specially treated 1-liter stainless steel (SS) and glass vessels. The sampling vessel and the sampling procedure are discussed in detail below. Typically, four samples--two with glass and two with stainless steel vessels--were collected at each site. Figure 1 shows the locations from which air was collected (Trip 1). The air samples were always collected at the cleanest possible locations under the most favorable meteorological conditions. A few urban samples were also collected. Trip 1 sampling continued from 15 September to 26 October 1977. These samples were analyzed after 26 October 1977.

Experiment 2

Air samples were collected on-board the U.S. Coast Guard ice breaker, Burton Island, which traveled from Oakland, California to Wellington, New Zealand, covering 36°N to 42°S latitude between 120°W and 175°E longitude. The actual itinerary is shown in Figure 1 (Trip 2). Air samples were collected in SS vessels, as in Experiment 1. This experiment

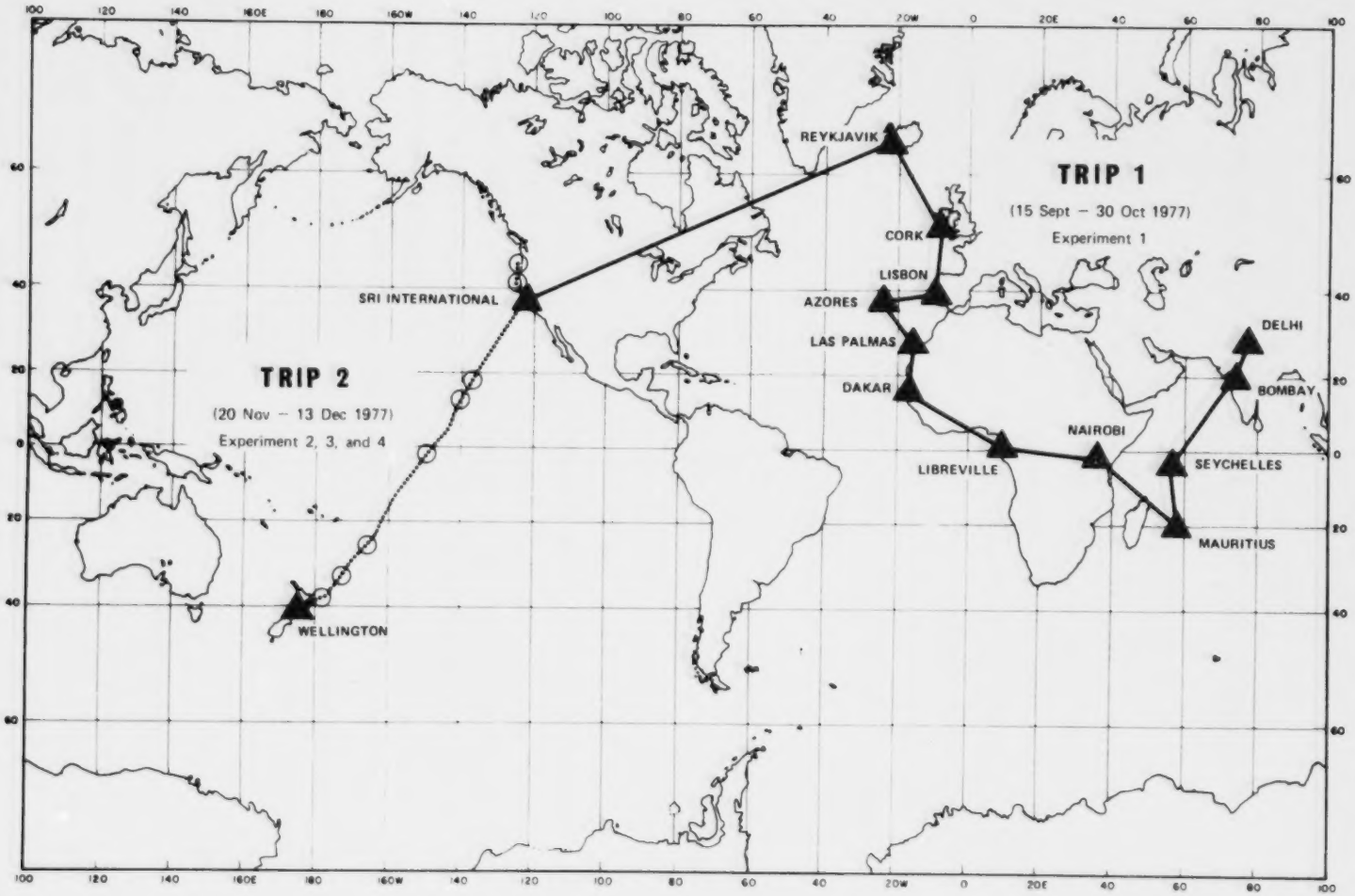

FIGURE 1 MAP SHOWING THE SAMPLING LOCATIONS FOR THE FOUR EXPERIMENTS

was conducted from 20 November to 13 December 1977, and these samples were later analyzed at our laboratories in Menlo Park.

Experiment 3

This experiment was conducted during the same oceanographic cruise and at the same time as Experiment 2. The major difference in Experiment 3, however, is that the air samples were analyzed in-situ with two 3920 Perkin Elmer gas chromatographs, each equipped with two electron-capture detectors and one flame ionization detector, and a coulometric gas chromatograph that were installed on-board.

WATER SAMPLING AND ANALYSIS

Experiment 4

Water samples from the Pacific Ocean were analyzed in-situ. Much of the water analysis was conducted on Trip 2. In addition, water samples from 40°N to 46°N in the Pacific Ocean were also analyzed. Seawater samples were collected from the surface (0 to 2 m) and from depths of 0 to 300 m at intervals of 50 m.

SAMPLING VESSELS

Both types of sampling vessels were so designed that they could be easily pressurized to 40 psi. Figures 2 and 3 show these sampling vessels. The stainless steel sampling vessels were electrochemically polished to have an inert surface and were commercially obtained from D and F instruments. The glass vessels were constructed at SRI International. Prior to use, they were heated to 250°C and flushed with ultra-pure helium that was cryogenically cleaned. A hundred volumes of the sampling vessel were exchanged over 100 minutes (helium flow rate $\approx$1 liter/minute). The sampling vessels were then checked for background contamination, and the procedure was repeated until the background contamination of the sampling vessels was reduced to less than 2 to 3% of the expected background concentration of a given trace constituent.

The sampling vessels were also placed in a contaminated room and rechecked for pressure stability and background contamination. Typically

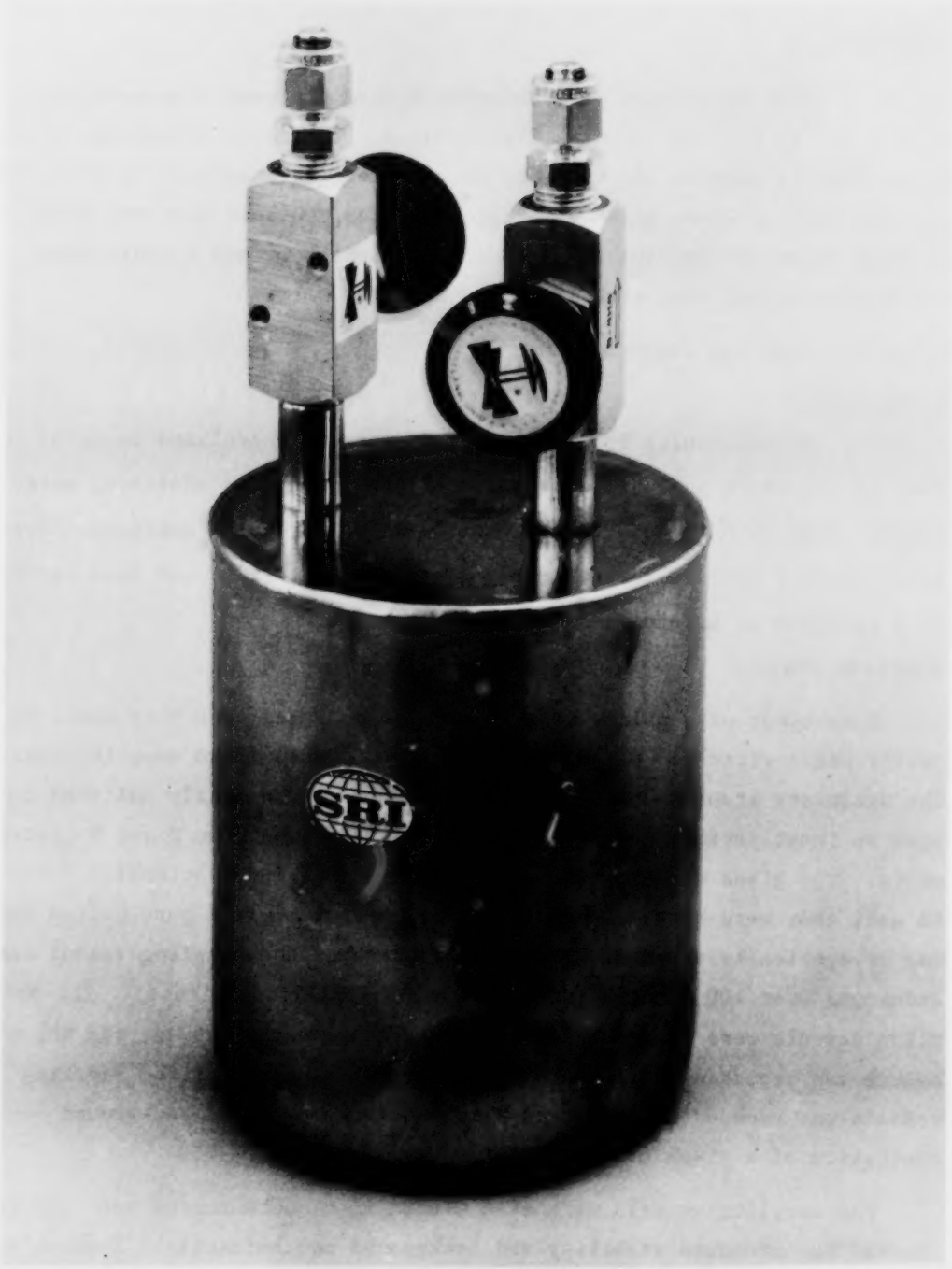

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FIGURE 2 STAINLESS STEEL CANISTERS FOR COLLECTING GRAB SAMPLES

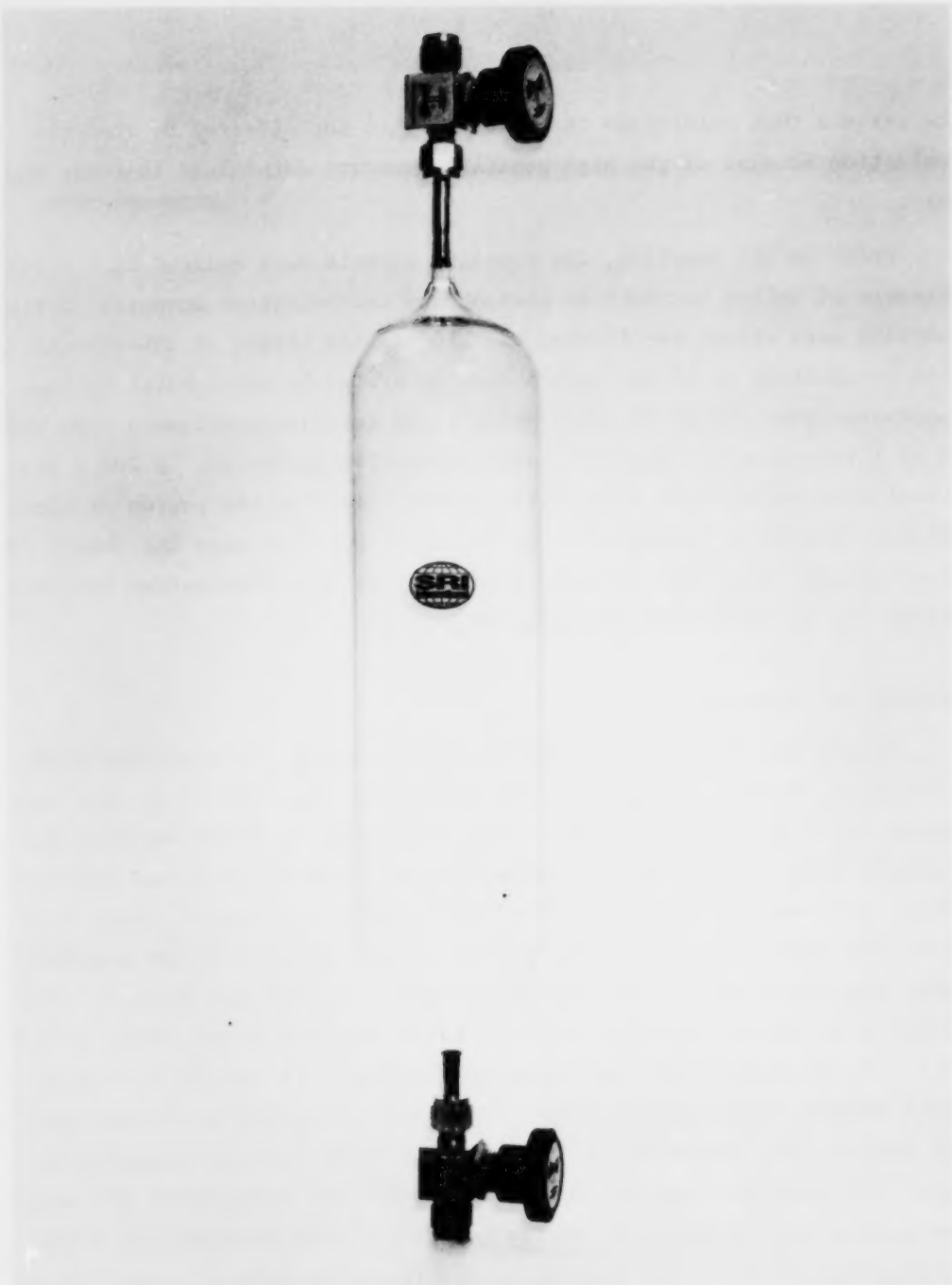

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FIGURE 3 ONE-LITER GLASS SAMPLING VESSEL

the vessels that maintained the pressure were not affected by room contamination because of the high positive pressure maintained in these vessels.

Prior to air sampling, the sampling vessels were carried at a positive pressure of helium (≈5 psi) to prevent any contamination enroute. During sampling each vessel was flushed with 100 to 150 liters of ambient air and then pressurized to 40 psi with a special stainless steel Metal Bellows compressor pump (Model MB 158), which could maintain continuous flow rate of 25 liters/minute. Figure 4 shows a sampling operation. A 200-m electrical cord was carried so we could sample away from the source of electricity, usually a farmhouse or an abandoned building near the ocean. Two blank samples were also carried to ensure that no contamination occurred during sample collection and analysis.

IN-SITU AIR SAMPLING

Aboard the Burton Island, in-situ air sampling was conducted using a stainless steel manifold with two inlet positions. We hoped that contamination from the ship exhaust could be avoided by switching from one manifold inlet to the other if meteorological conditions turned unfavorable. Both manifold inlets were at the front of the vessel, about 10 m above sea level and 20 m apart. At any given instant only the manifold inlet that would obtain the cleanest possible air was operational. The decision to select the right manifold inlet was made on the basis of wind data. On extremely calm days (wind speed <5 mph) it was impossible to avoid exhaust contamination from either of the sampling manifolds, and air samples were collected in glass syringes from the best possible location. If clean air samples could not be obtained, analysis of air samples was terminated. Because the Burton Island is round-bottomed and rolls excessively, we could not monitor on highly stormy days.

All air samples were analyzed for halocarbons, light hydrocarbons, N_2O, and SF_6. The methods of analysis have been published elsewhere (Singh et al., 1977a, 1977b, and 1977c). Electron capture gas chromatography was used for all species except the hydrocarbons, for which

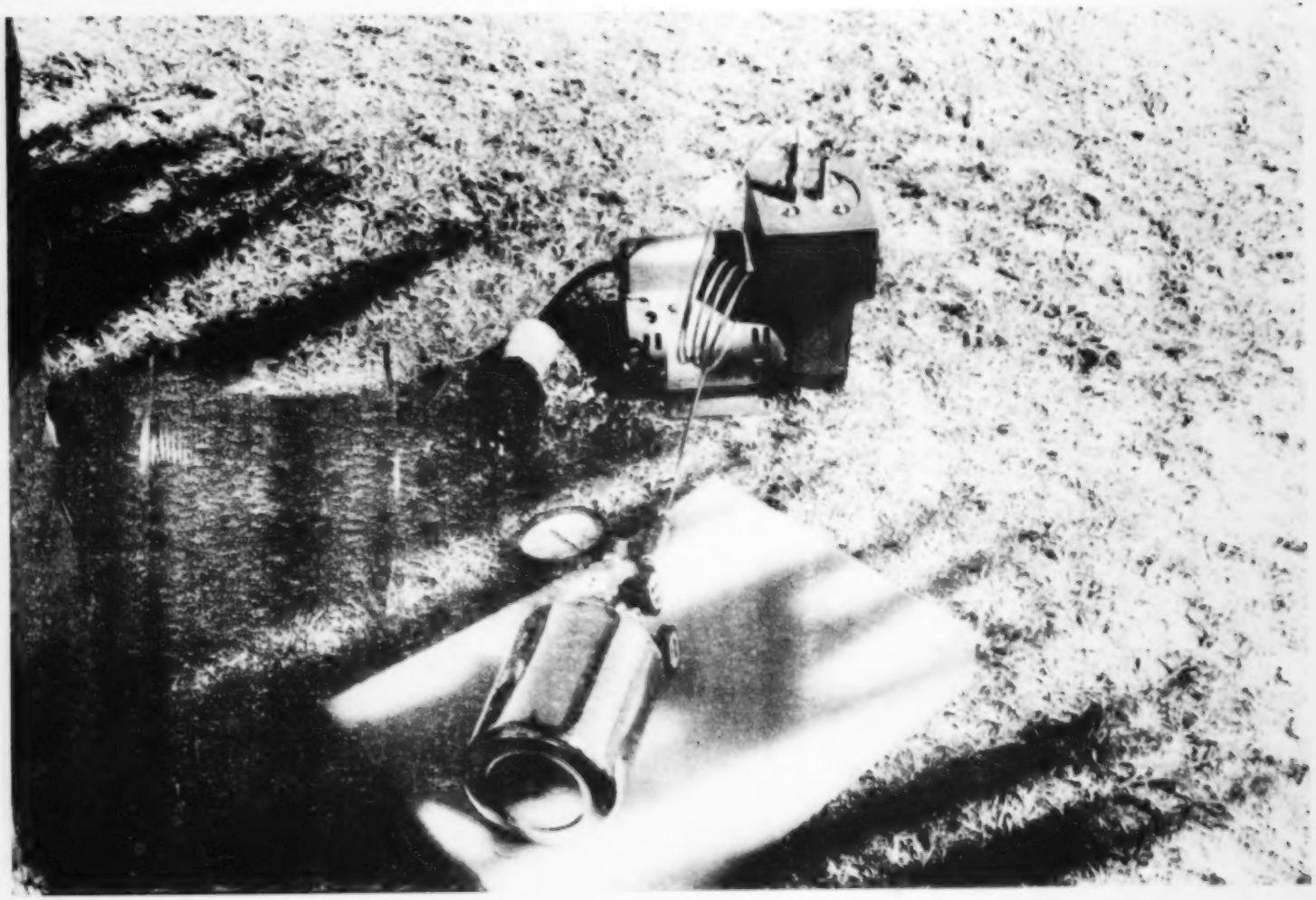

FIGURE 4 AIR SAMPLING IN STAINLESS STEEL VESSEL

flame ionization detector (FID) was used. Cryogenic preconcentration of air samples was conducted at liquid oxygen temperature prior to analysis. Typically, sample size was less than 500 ml. In some instances, direct 5-to-10-ml air injections were used; for example, cryogenic analysis was not necessary for N_2O. Secondary standards were routinely analyzed to monitor any changes in instrument responses. In the case of N_2O ultra high precision was sought, so each air injection was accompanied by a standard air injection. The hydrocarbon primary standards were obtained from Scott-Merrion.

WATER SAMPLING

The task of water sampling from depths of 0 to 300 m was handled by the Burton Island crew. Paired samples were obtained from 0 to 300 m at 50-m intervals. Water temperature at these depths was also measured. Each water sample provided 0.5 liters of seawater and was usually analyzed within an hour or two of collection. Figure 5 shows the water sampling being conducted. Water sample analysis was conducted by equilibrating the water with an equal volume of ultra clean air. The constituent of interest was then analyzed in air, and the corresponding equilibrium concentration in water was calculated from available solubility data. The trace constituents in air and water were then added to obtain the water concentration.

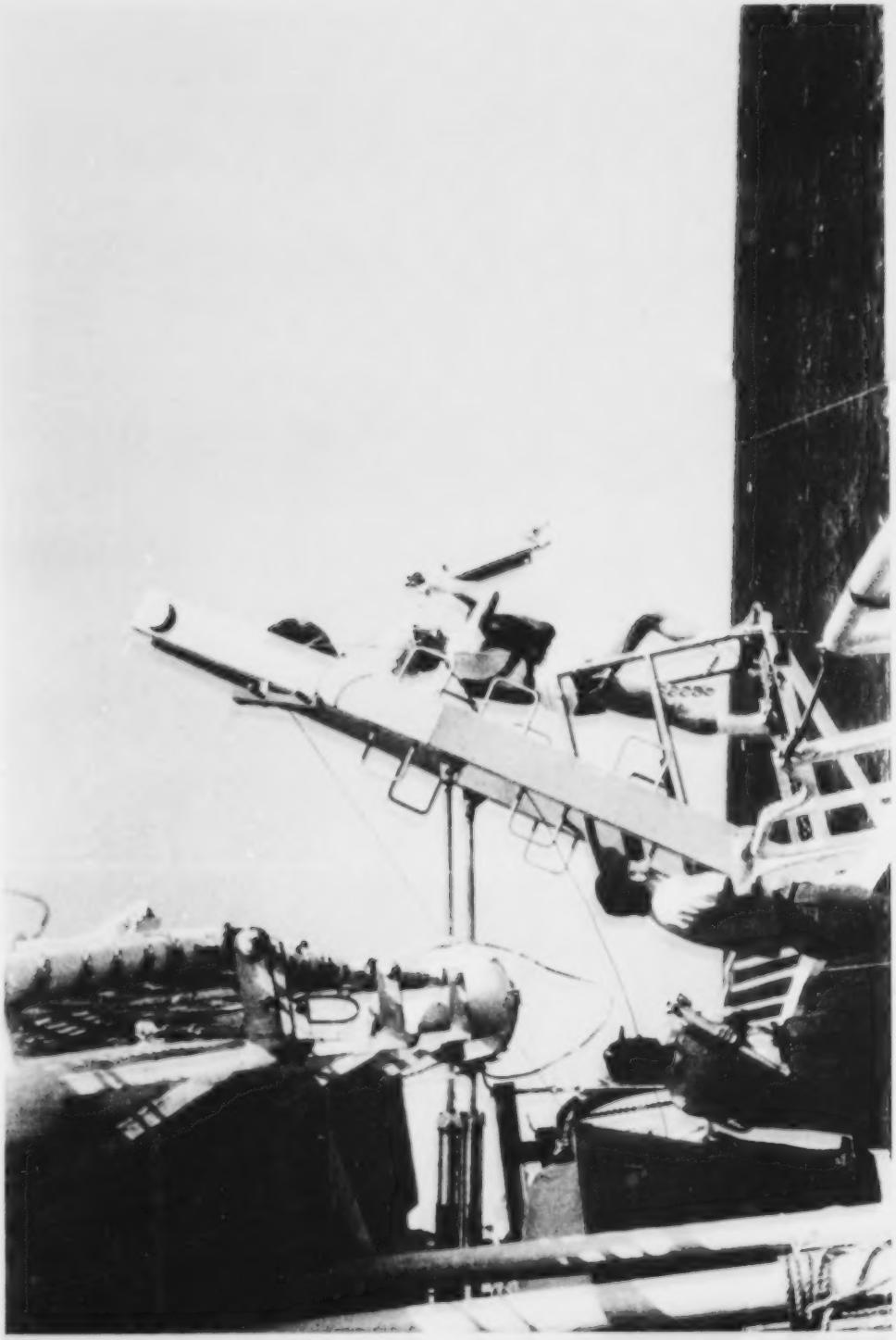

FIGURE 5 DEEPWATER SAMPLING IN THE PACIFIC OCEAN

ATMOSPHERIC ABUNDANCE AND VARIABILITY OF TRACE CONSTITUENTS

The experiments went satisfactorily at all sites, and no serious problems were encountered. Stormy weather occasionally made it impossible to operate on the oceanographic cruise, but such days were few. Some of the glass containers were broken enroute to SRI due to airline handling, but during Trip 1 samples were collected in quadruplicate, so these handicaps did not pose any serious problem. Samples that clearly showed signs of contamination were discarded. Two urban samples collected from Lisbon were treated separately. The analysis of data reported here is by no means complete. Additional analyses will appear in future reports and publications.

In the figures showing the atmospheric distribution of trace constituents the following symbols have been used to identify the sampling techniques used to obtain the data:

- ▽ Trip 1, Experiment 1, stainless steel vessels
- △ Trip 1, Experiment 1, glass vessels
- ◇ Trip 2, Experiment 2, stainless steel vessels
- □ Trip 2, Experiment 3, in-situ air sampling and analysis

Table 3 summarizes the data on background concentrations of the measured trace constituents in the northern and southern hemispheres. For species that showed concentration gradients within each hemisphere, the average background concentration is defined as the concentration that, when present uniformly in one hemisphere, represents the total burden of a given pollutant in that hemisphere. To derive this uniform background concentration a weighted average of the latitudinal concentration variation has been taken. A third-order polynomial was fitted to all of the data, and the polynomial coefficients for each constituent are shown in Table 4. In the calculations of averages and the polynomial fit, visible outliers are deleted.

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Table 3

SUMMARY OF THE AVERAGE CONCENTRATIONS OF MEASURED TRACE CONSTITUENTS

Compound	Concentration (ppt)*		
	N.H. Average	S.H. Average	Global Average
N_2O	311×10^3 (2.3×10^3)†	311×10^3 (2.8×10^3)	311×10^3
CCl_2F_2 (F12)	230 (25.5)	210 (25.1)	220
CCl_3F (F11)	133 (13.4)	119 (11.7)	126
CCl_2FCClF_2 (F113)	19 (3.5)	18 (3.1)	18
$CClF_2CClF_2$ (F114)	12 (1.9)	10 (1.3)	11
$CHCl_2F$ (F21)	5 (2.6)	4 (1.0)	4
SF_6	0.31 (0.04)	0.27 (0.01)	0.29
CCl_4	122 (4.9)	119 (4.0)	120
CH_3CCl_3	113‡	75‡	94
CH_3Cl	611 (83.7)	615 (103.0)	613
CH_3I	2 (1.0)	2 (1.2)	2
$CHCl_3$	14 (7.0)	≤ 3	8
CH_2Cl_2	44 (14.0)	20 (4.0)	32
C_2HCl_3	16 (8.0)	<3	8
C_2Cl_4	40 (12.0)	12 (3.0)	26
CH_4	1430×10^3 (64.7×10^3)	1390×10^3 (51.4×10^3)	1410×10^3
C_2H_6	1060‡	524 (14.8)	792
C_2H_2	<200	<200	<200

*ppt = 10^{-12} v/v.

†Parentheses indicate standard deviation.

‡For those species where significant variations within each hemisphere were observed, the average concentration within each hemisphere is the concentration that, when uniformly mixed within the hemisphere, represents the total burden of the species in that hemisphere.

Table 4

LEAST-SQUARES ERROR COEFFICIENTS OF A THIRD-ORDER POLYNOMIAL USED TO DEFINE THE GLOBAL DISTRIBUTION OF TRACE CONSTITUENTS

Compound	Coefficients of Polynomial*			
	a	b	c	d
N_2O	3.112 (2)†	-1.451 (-2)	-3.325 (-4)	-8.675 (-8)
CCl_2F_2 (F12)	2.206 (2)	0.363	1.096 (-3)	-1.574 (-5)
CCl_3F (F11)	1.290 (2)	0.498	-3.178 (-3)	-8.510 (-5)
CCl_2FCClF_2 (F113)	1.787 (1)	5.249 (-2)	2.346 (-4)	-6.662 (-6)
$CClF_2CClF_2$ (F114)	1.153 (1)	5.591 (-2)	-4.059 (-4)	-7.693 (-6)
$CHCl_2F$ (F21)	4.212	2.952 (-2)	5.583 (-5)	-3.038 (-6)
SF_6	0.292	9.221 (-4)	-5.817 (-6)	1.370 (-7)
CCl_4	1.198 (2)	4.412 (-2)	6.337 (-4)	4.967 (-6)
CH_3CCl_3	8.971 (1)	0.818	7.584 (-4)	-7.894 (-5)
CH_3Cl	6.190 (2)	0.697	-3.128 (-3)	-1.204 (-4)
CH_3I	1.711	-9.422 (-3)	6.931 (-4)	-5.878 (-6)
CH_4	1.409 (3)	0.828	4.435 (-5)	-8.113 (-5)
C_2H_6	0.769	9.926 (-3)	6.526 (-5)	5.561 (-8)

*The polynomial is $Y = a+bL+CL^2+dL^3$, where Y is the concentration in ppt for all species except N_2O, CH_4, and C_2H_6, for which it is ppb. The independent variable L is the latitude in degrees and varies from -90° to +90° (N.H. = 0 to +90°, S.H. = 0 to -90°).

†3.112 (2) = 3.112×10^2.

The hemispheres are by no means well mixed when one is dealing with reactive species, and we wish to emphasize that data collected during this study are ground-level data. Except in a few instances it is safe to assume, however, that no significant vertical concentration gradients exist. This has been shown by Cronn et al. (1976). In the following discussion, we shall consider the atmospheric abundance and distribution of the measured trace constituents in greater detail.

NITROUS OXIDE

Figure 6 shows the distribution of N_2O between 63°N and 90°S. It seems clear that no significant variation exists. The following data are most important:

Average N_2O concentration in the N.H. = 311 ± 2.8 ppb
Average N_2O concentration in the S.H. = 311 ± 2.3 ppb
Average global N_2O concentration = 311 ± 2.6 ppb

Thus we calculate a 311 ppb N_2O concentration in the globe with a 0.8% overall standard deviation (σ_t). Part of this variability is due to the precision of our analysis, which was determined to be within about 0.3% (σ_p), with standard air samples. Such high precision can be obtained only if each air injection is followed by a standard air injection and the effects of relative humidity (R.H.) are carefully subtracted. The data on N_2O presented here has been corrected to a constant R.H. of 50%. The R.H. corrections were made based on 3-hour average R.H. values. All samples analyzed within a given 3-hour period were subject to the same correction. Samples collected on Trip 1 were not corrected for R.H., but a gas chromatographic check indicated that the R.H. was probably not far from 50% and that these errors could not be more than 0.2% ($\sigma_{R.H.}$). The real variance (σ_a^2) due to atmospheric variability can be defined as:

$$\sigma_a^2 = \sigma_t^2 - \sigma_p^2 - \sigma_{R.H.}^2$$

$$= (0.8)^2 - (0.3)^2 - (0.2)^2 = (0.7)^2 \quad . \qquad (2)$$

Thus, an atmospheric variation of about 0.7% (σ_a) can be calculated. Using the formula derived by Junge (1974), a residence time estimate for N_2O can be obtained:

$$\tau_{est} = \frac{14}{\sigma_a} = 20 \text{ years} \quad . \qquad (3)$$

However, as Hahn and Junge (1976) have stated, this estimate is probably low by as much as a factor of 3, primarily because the atmospheric variability of N_2O are approaching the precision of our analysis and the true variability is probabily less than 0.7%. An additional factor also must be

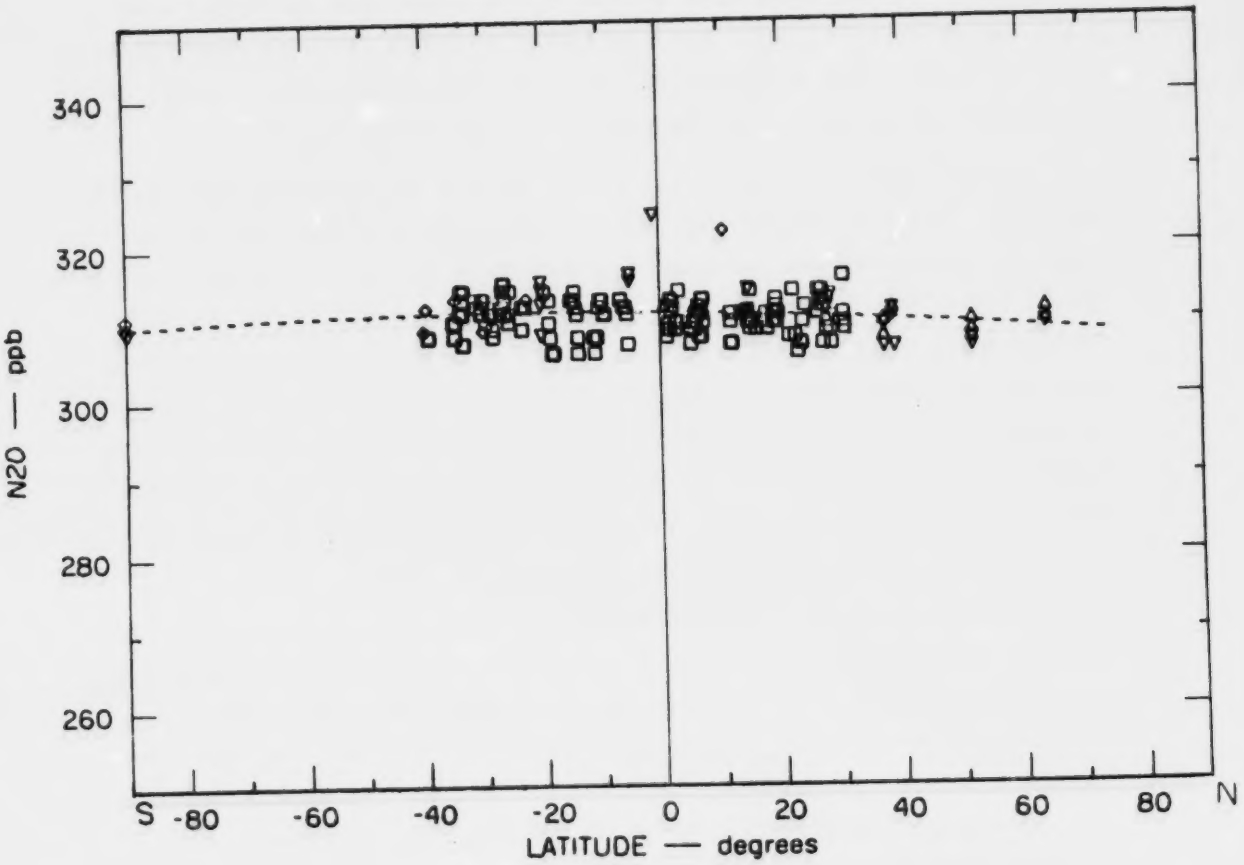

FIGURE 6 GLOBAL DISTRIBUTION OF N_2O

considered. All of our data were collected within 15 m of the ocean surface; for this reason a greater N_2O variability can be expected because the ocean was supersaturated with N_2O (see Section VI-A). Thus the possibility that the residence time of N_2O in the atmosphere is 20 x 3 = 60 years cannot be ruled out. Data collected by Weiss (private communication of R. F. Weiss, Scripps Oceanographic Institute, California) support an upper limit of 84 years for the residence time of N_2O (σ_a = 0.5%).

Figure 7 shows a plot of N_2O levels at several locations between 1975 and 1977. The mean values show that no significant change ($\approx$0.3% per year) in the atmospheric abundance of N_2O has occurred during this period (Table 5). The standard deviations, however, are quite large, probably because extra care was not taken to obtain high precision, since such a need was not identified. Typically, calibration standards were injected infrequently, and this is probably the single most important reason for higher standard deviations. In the past, corrections for R.H. changes, which could account for an error as large as ±0.5%, were also not made.

To remedy these deficiencies, air samples collected in 1975 were compared with air samples collected and analyzed during Trip 2. Two samples of clean air collected in September 1975 at a clean coastal site in California ($\approx$40°N) were used. The N_2O in these 1975 samples was compared with that in ambient air between 24°N and 35°S. Extreme care was taken to obtain maximum precision. Since the R.H. in the two samples of 1975 air was measured only roughly at about 50%, all ambient measurements of N_2O were reduced to the 50% R.H. value.

Table 6 shows the N_2O levels in the September 1975 air sample and in ambient air. It is clear that the average N_2O concentration of 311.8 ppb in December 1977 is about 0.2% less than the September 1975 value of 312.3 ppb. If one considers the standard deviations around the mean, a change of +0.5% to -0.8% in the atmospheric abundance of N_2O over a 27-month period can be calculated. Since this change is within the atmospheric variability of N_2O, a more definitive conclusion cannot be drawn. We can, however, safely conclude that no significant change (±0.5%) in the atmospheric abundance of N_2O over the last two years has occurred. This is contrary to the changes projected by Crutzen (1976), and

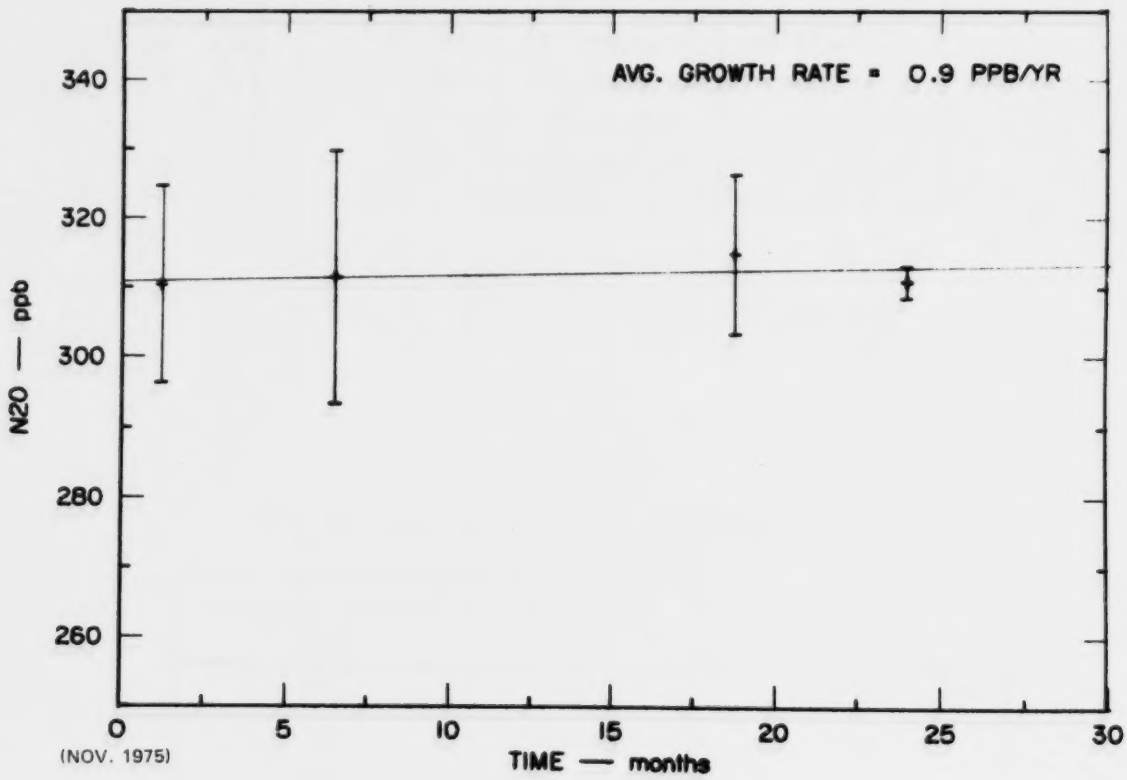

FIGURE 7 GROWTH OF N_2O WITH TIME

Table 5

AVERAGE ATMOSPHERIC GROWTH RATES OF IMPORTANT SPECIES FROM NOVEMBER 1975 TO DECEMBER 1977

Compound	Average Growth Rate*	
N_2O	0.9 ppb/yr†	0.3 ($\approx$0) %/yr
CCl_2F_2 (F12)	18.5 ppt/yr	10%/yr
CCl_3F (F11)	12.9 ppt/yr	12%/yr
CCl_4	2.3 ppt/yr	2 %/yr
CH_3CCl_3	15.5 ppt/yr	17%/yr

*Based on data collected between 35°N - 40°N.

†More precise comparisons indicate an average change of -0.1% per year (see Table 6).

Table 6

AMBIENT N_2O CONCENTRATIONS (ppb) IN 1975 AND 1977

Latitude	September 1975	November-December 1977
24°N	312	310
18°N	311	312
14°N	313	313
4°N	312	311
1°N	313	312
4°S	313	312
15°S	313	313
25°S	312	310
30°S	313	313
35°S	311	312
Average concentration ($\pm\sigma$)	312.3 ± 0.81	311.8 ± 1.14

McElroy et al. (1976). It is possible, however, that the relative yield of N_2O during denitrification is significantly lower than the current estimates of 7 to 50% (Crutzen, 1976; Hahn and Junge, 1977). It is also possible that the soil is not a source of N_2O and that application of fertilizer is likely to have virtually no impact on the atmospheric abundance of N_2O. This hypothesis is developed further in Section VI.

FLUORINATED TRACE CONSTITUENTS

Six important fluorinated species--CCl_2F_2 (F12), CCl_3F (F11), CCl_2FCClF_2 (F113), $CClF_2CClF_2$ (F114), $CHCl_2F$ (F21), and SF_6--were measured. While data on F21 have been provided, we are not sure if F21 is an experimental artifact or a true atmospheric constituent. Therefore, all data on F21 must be considered tentative.

Fluorocarbon 12

Figure 8 shows the latitudinal variation of F12. A third-order polynomial fits the data well. F12 is nearly uniformly mixed in the southern and northern hemispheres. The following data were obtained:

Average F12 concentration in the N.H. = 230 ± 25.5 ppt
Average F12 concentration in the S.H. = 210 ± 25.1 ppt
Average global F12 concentration = 220 ppt

Thus there is a north-south gradient, with the S.H. average concentrations about 9.5% less than the N.H. values. The data support our observation that F12 is well mixed at least within each hemisphere. Using a simplified two-box model approach previously developed (Singh, 1977b), we can easily conclude that the interhemispheric exchange time must be less than 1.3 year. While detailed calculations will be presented later, the data in Figure 8, when coupled with extrapolated emissions data provided by E. I. DuPont de Nemours and Company (1977), do not disagree significantly with a 50-year residence time calculated by Singh (1977a).

Figure 9 shows the growth rate of atmospheric F12 calculated over a 27-month period. This growth rate of 18.5 ppt/year (≈10% per year) is reasonably consistent with the actual growth in the F12 emissions. The growth data are summarized in Table 5.

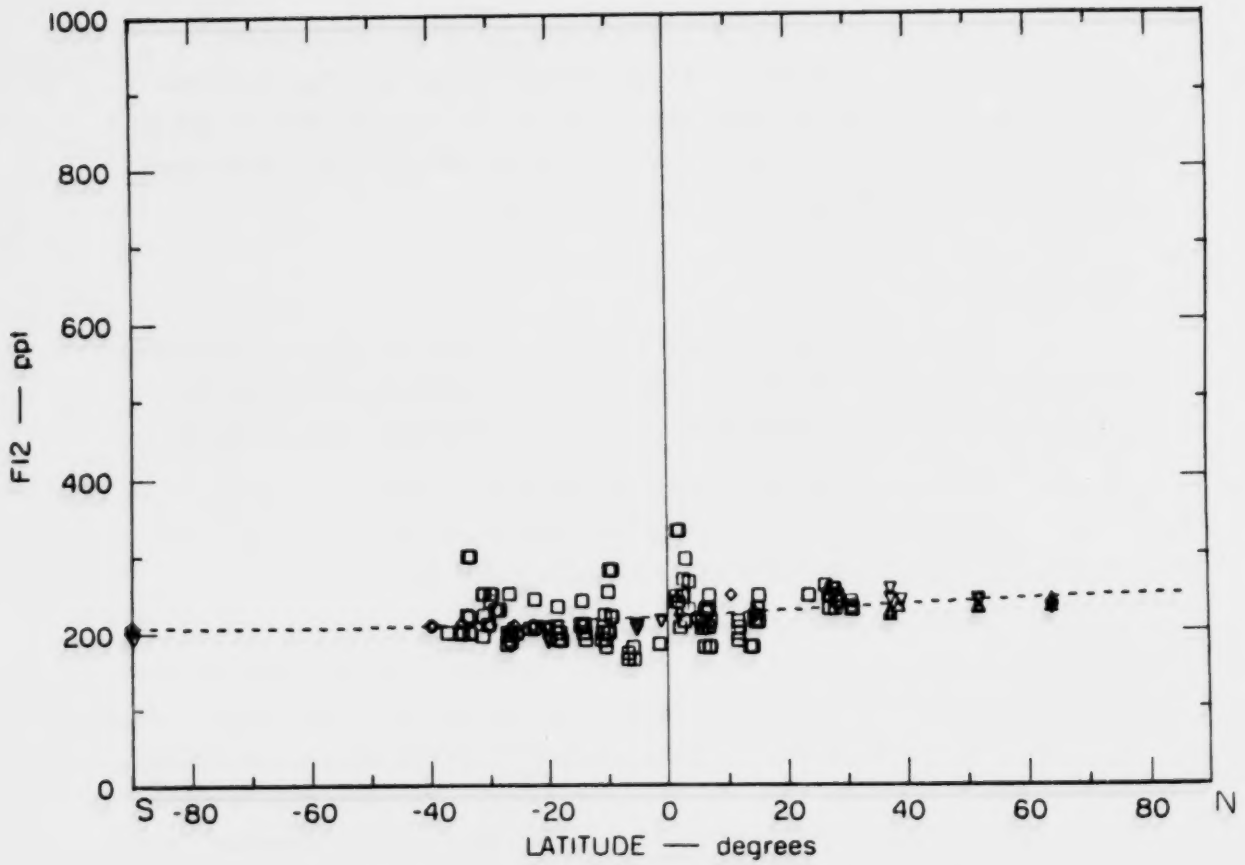

FIGURE 8 GLOBAL DISTRIBUTION OF F12

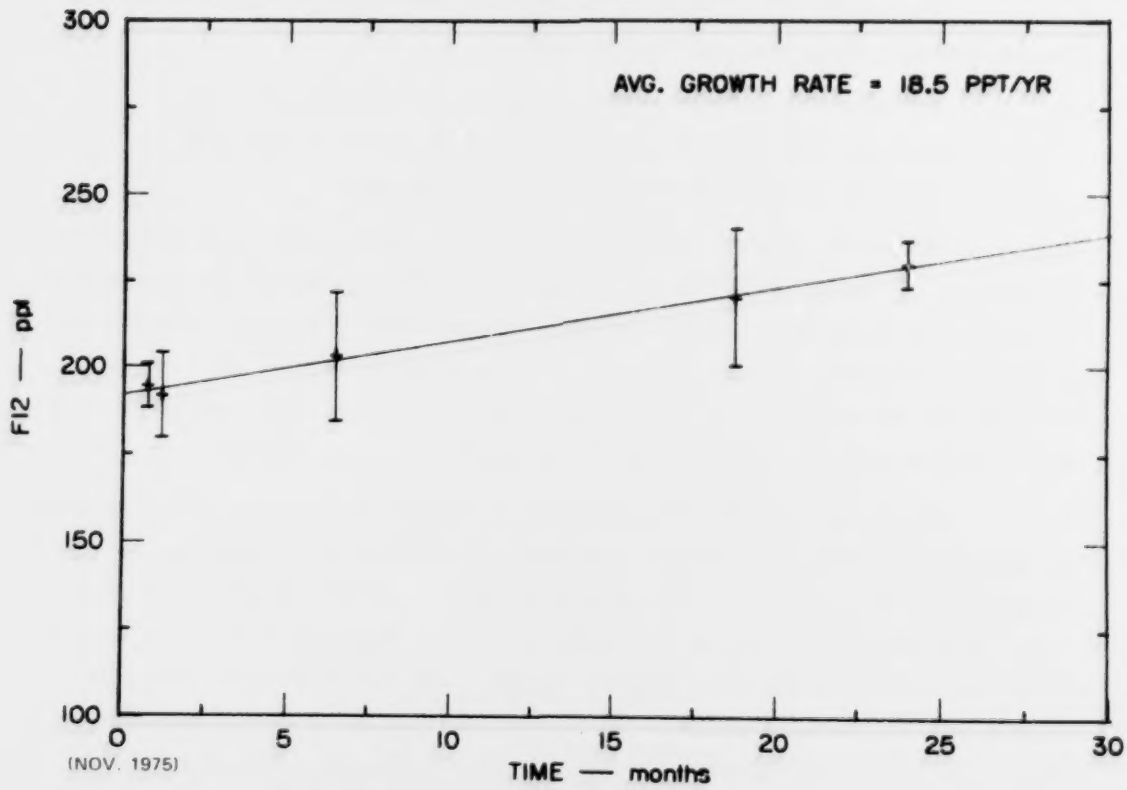

FIGURE 9 GROWTH OF F12 WITH TIME

The urban samples of F12 from Lisbon contained F12 in concentrations of about 800 ppt. Similar urban concentrations have also been reported in the U.S. (Singh, et al., 1977b, 1977c).

Fluorocarbon 11

The global distribution of F11 was ver similar to that of F12. The following concentrations were obtained:

Average F11 concentration in the N.H. = 133 ± 13.4 ppt
Average F11 concentration in the S.H. = 119 ± 11.7 ppt
Average global F11 concentration = 126 ppt

Figure 10 shows the global variation of F11; a north-south concentration difference of about 10.5% can be calculated. This gradient is consistent with an interhemispheric exchange rate of less than 1.3 year. Figure 11 clearly shows that, on the average, F11 has increased at a rate of 12.9 ppt/year (≈12% per year). This rate of growth agrees with available emissions data when a residence time of 30 to 40 years is assumed.

Our measured F11 distribution is inconsistent with that reported by Lovelock (1973), but agrees reasonably well with data reported by Rasmussen et al. (1976). The calculated burden of F11 based on the north-south distribution provided by Lovelock (1973) suggests much lower concentrations of F11 in the S.H. than we found. The net effect of using F11 concentrations lower than ours is that in any analysis of F11 residence time, unusually low residence times can be calculated. This is a major cause of disagreement between the residence time of 10 to 20 years calculated by Jesson et al. (1977) and that of 30 to 45 years calculated by Singh (1977a).

Fluorocarbon 113

The latitudinal distribution of F113 is shown in Figure 12; a third-order polynomial fit is also shown. The following data were calculated:

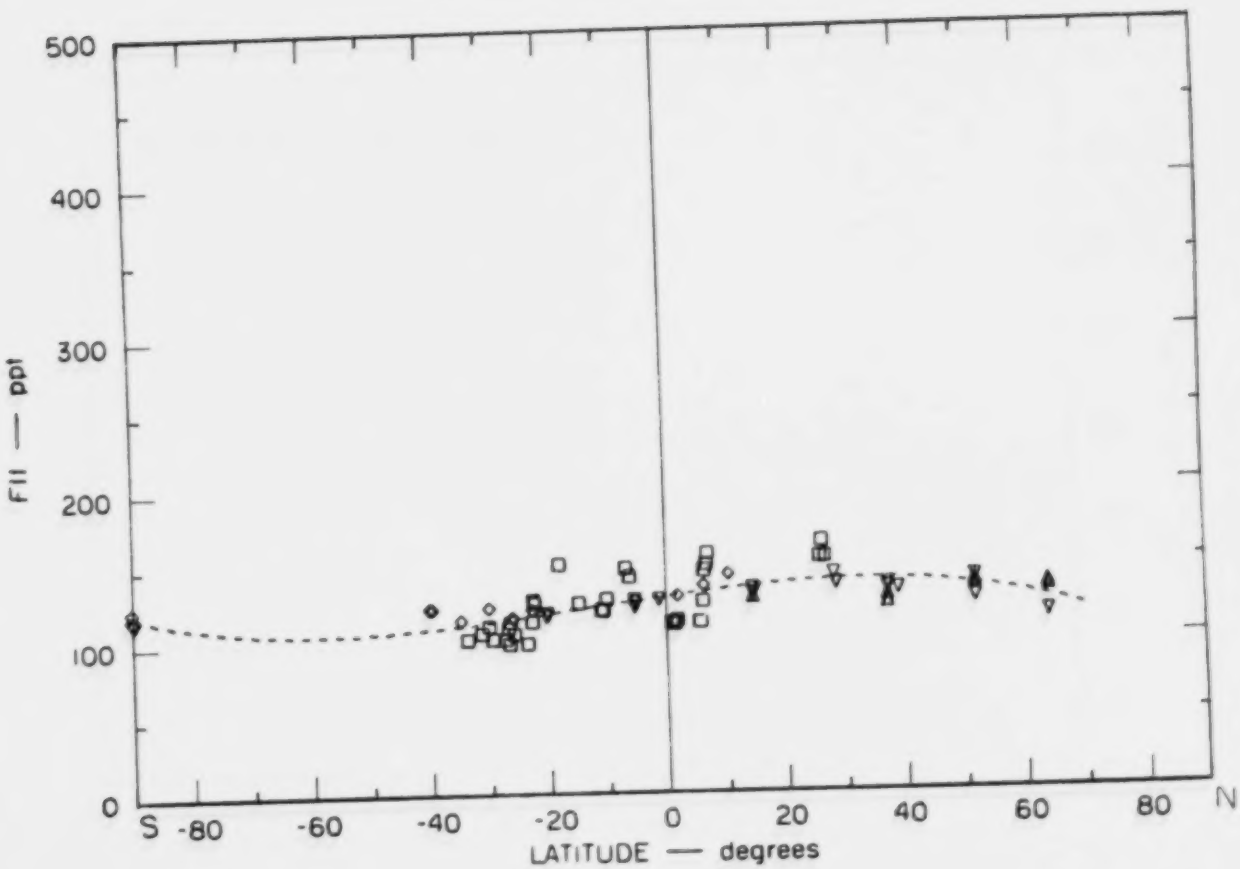

FIGURE 10 GLOBAL DISTRIBUTION OF F11

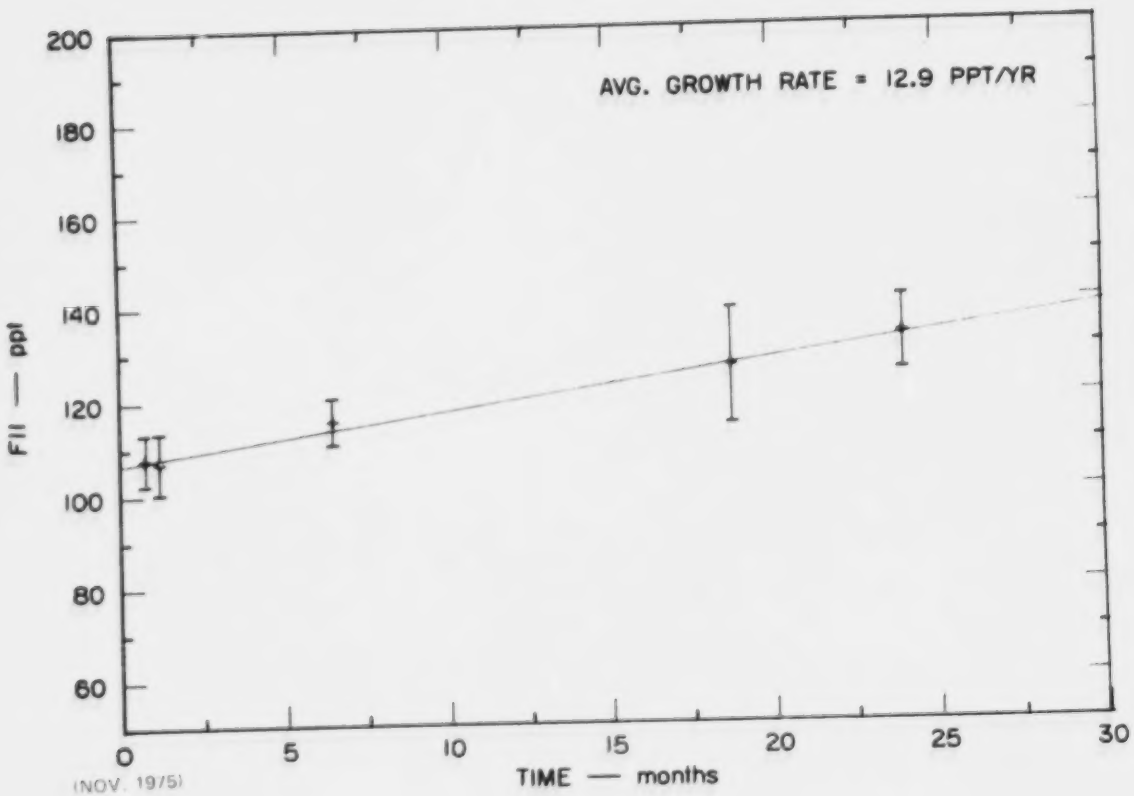

FIGURE 11 GROWTH OF F11 WITH TIME

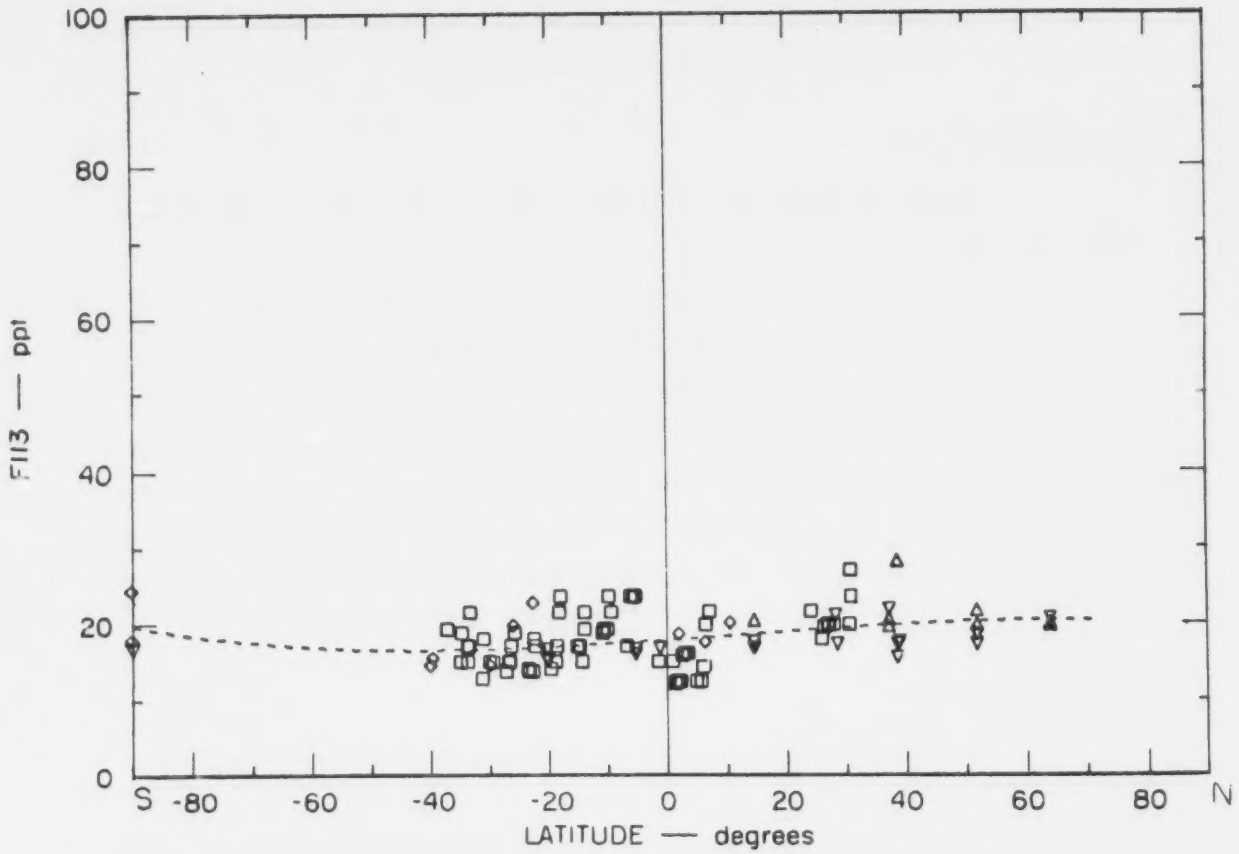

FIGURE 12 GLOBAL DISTRIBUTION OF F113

Average F113 concentration in the N.H. = 19 ± 3.5 ppt
Average F113 concentration in the S.H. = 18 ± 3.1 ppt
Average global F113 concentration = 18 ppt

A north-south concentration difference of about 5% was found. Accurate emissions data on F113 are not currently available, but the residence time of F113 should be similar to those of F11 and F12. We calculate the 1978 global burden of F113 to be 0.6 million tons.

Fluorocarbon 114

Figure 13 shows the latitudinal variation of F114. The following data were obtained:

Average F114 concentration in the N.H. = 12 ± 1.9 ppt
Average F114 concentration in the S.H. = 10 ± 1.3 ppt
Average global F114 concentration = 11 ppt

The global average concentration corresponds to a burden of 0.3 million tons. Accurate emissions data for F114, however, are also not available. Reasonable estimates suggest that the measured F114 burden is comparable to cumulative F114 emissions. A hemispheric concentration difference of 16% is also consistent with a fast interhemispheric exchange rate.

Fluorocarbon 21

As stated earlier, we cannot yet confirm that F21 is a true atmospheric constituent or an experimental artifact. The global distribution of F21 is shown in Figure 14. The average concentration is about 4 ppt. The lack of a large gradient in the N.H. and S.H. for a species with such a low atmospheric residence time suggests that it may be an artifact, but we were unable to determine its nature. Thus the following data are tentatively presented:

Average F21 concentration in the N.H. = 5 ± 2.6 ppt
Average F21 concentration in the S.H. = 4 ± 1.0 ppt
Average global F21 concentration = 4 ppt.

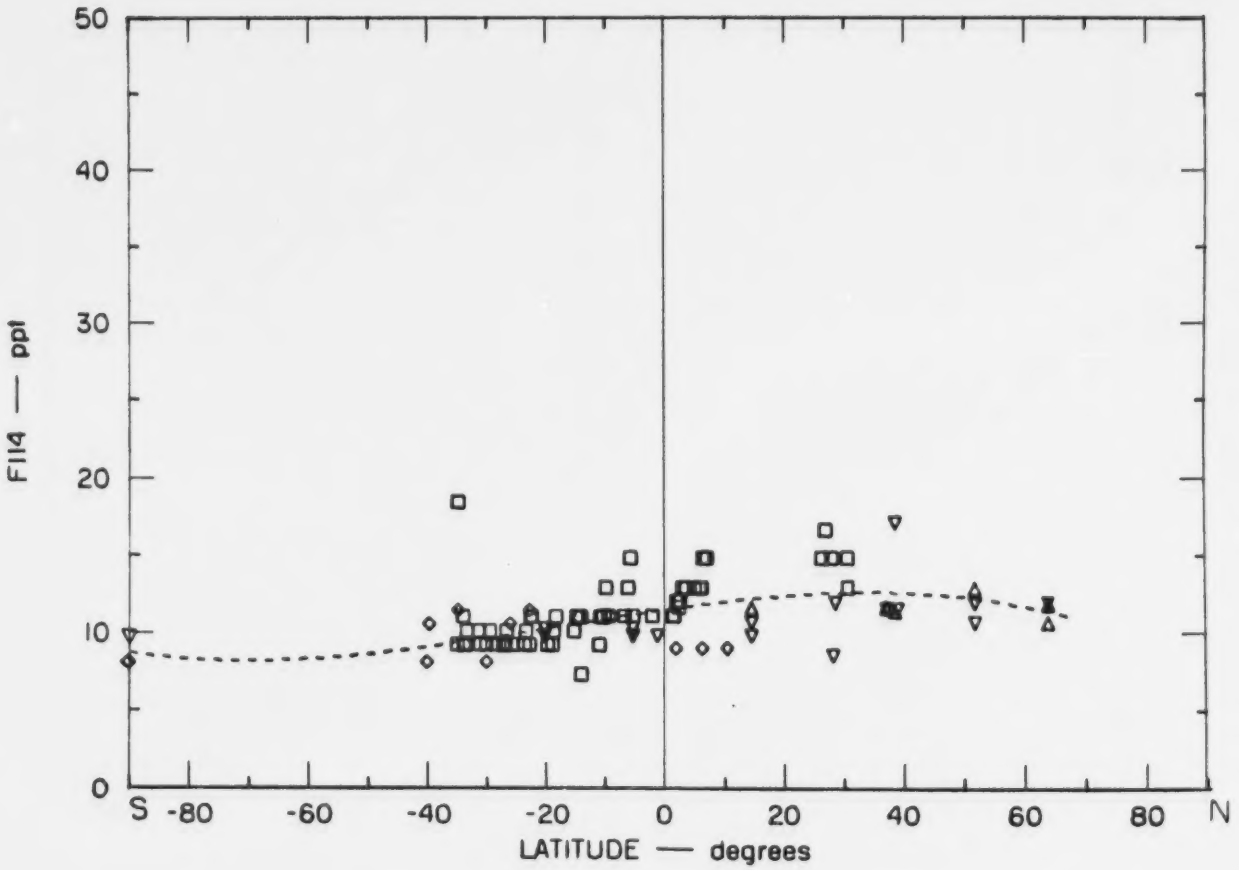

FIGURE 13 GLOBAL DISTRIBUTION OF F114

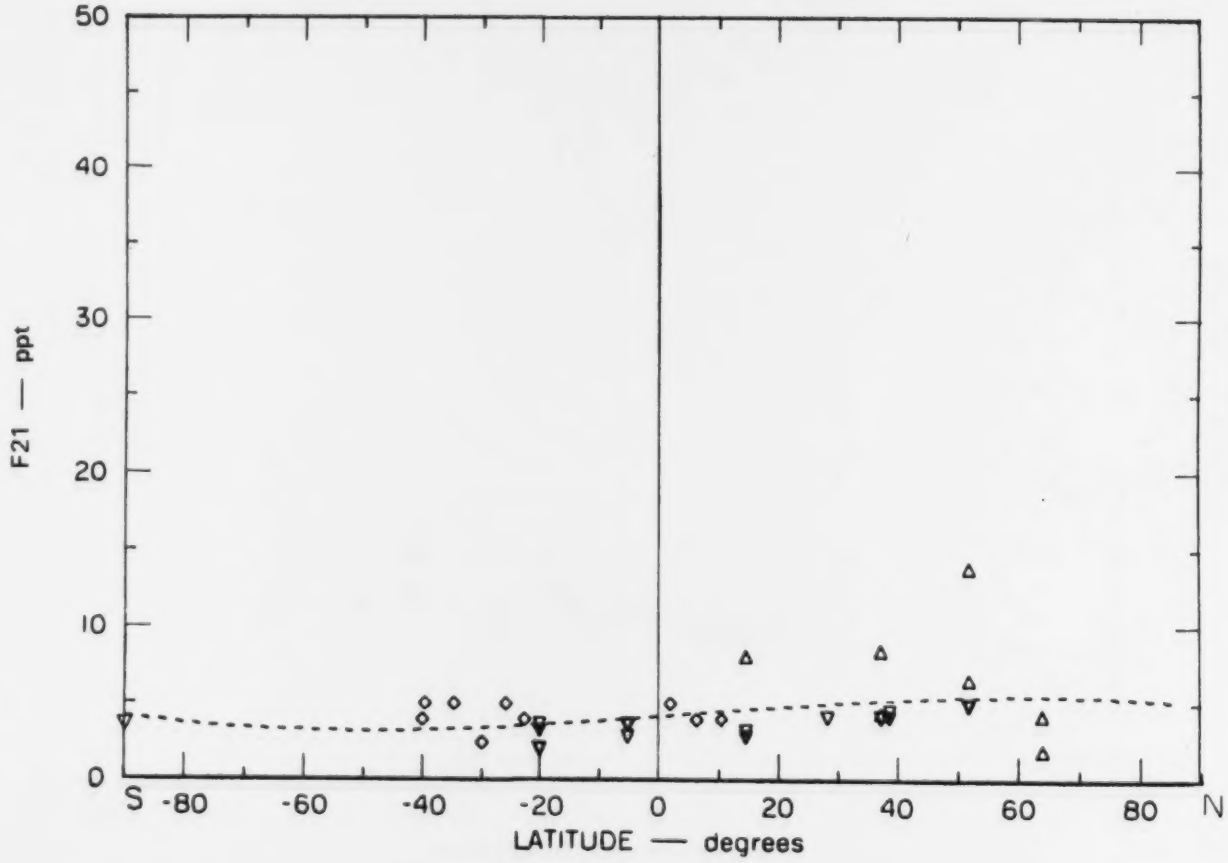

FIGURE 14 GLOBAL DISTRIBUTION OF F21

Sulfur Hexafluoride

We have earlier reported a background concentration of SF_6 and about 0.28 ppt in the northern hemisphere (Singh et al., 1977b and 1977c). Because of the very low concentration of SF_6, extensive data from other sources have not been available. Figure 15 shows the latitudinal distribution of SF_6 and its concentration in the northern and southern hemispheres. The following data can be reported:

Average SF_6 concentration in the N.H. = 0.31 ± 0.04 ppt
Average SF_6 concentration in the S.H. = 0.27 ± 0.01 ppt
Average global SF_6 concentration = 0.29 ppt

The hemispheric gradient of SF_6 of about 13% supports the hypothesis that SF_6 is farily well mixed in the atmosphere. The atmospheric burden of SF_6 can be calculated to be about 7 thousand tons. Because SF_6 has a much longer lifetime than either F12 or F11, it is an excellent tracer of global mixing processes. Continued emissions of, and increases in, SF_6 could result in deposition of sulfur at altitudes above 50 km with unknown effects.

OTHER HALOGENATED TRACE CONSTITUENTS

Eight other atmospheric trace constituents--CCl_4, CH_3CCl_3, CH_3Cl, CH_3I, $CHCl_3$, CH_2Cl_2, C_2HCl_3, and C_2Cl_4--were measured. Reliable data for both northern and southern hemisperes were obtained only for the first four. Some sample contamination occurred in our sampling vessels for the others.

Carbon Tetrachloride

Unlike fluorocarbons, CCl_4 is rather uniformly distributed around the globe (Figure 16). This is not surprising, since emissions of CCl_4 in the last decade have been very small, and the concentration is fairly uniform. A very small difference of about 2.5% exists between the N.H. and S.H. burdens of CCl_4. The following data were obtained:

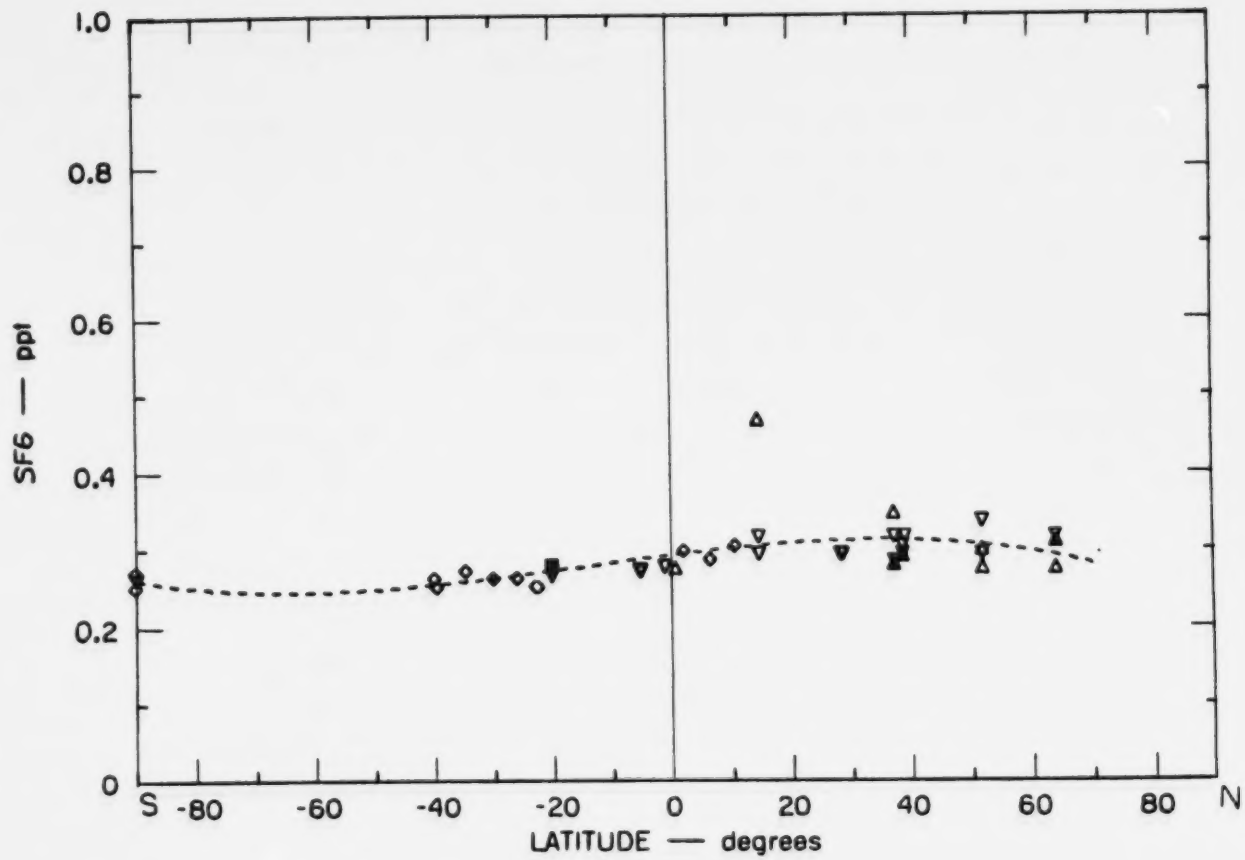

FIGURE 15 GLOBAL DISTRIBUTION OF SF_6

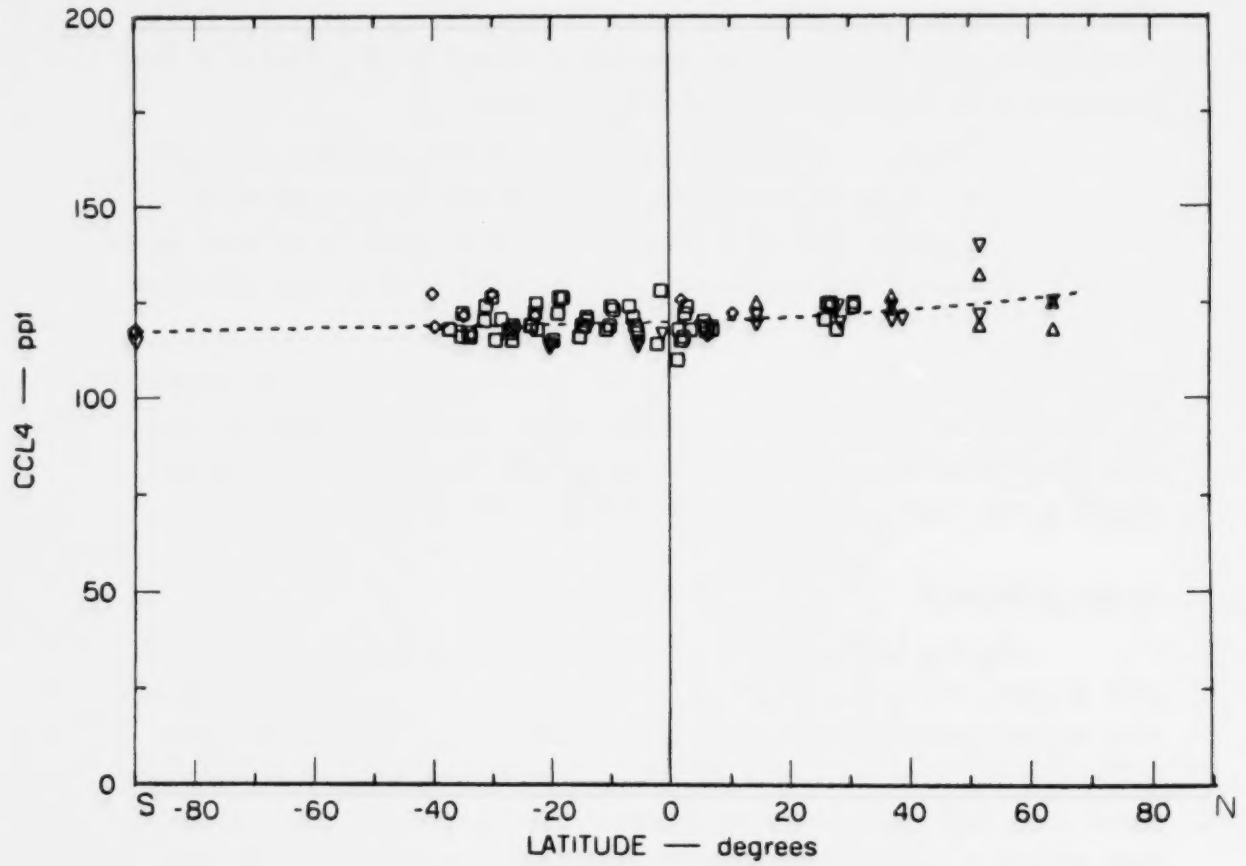

FIGURE 16 GLOBAL DISTRIBUTION OF CCl_4

Average CCl_4 concentration in the N.H. = 122 ± 4.9 ppt
Average CCl_4 concentration in the S.H. = 119 ± 4.0 ppt
Average global CCl_4 concentration = 120 ppt

The background concentration of CCl_4 indicates a global burden of 3.2 million tons. Our calculated burden of CCl_4 is somewhat higher than the estimated emissions data compiled by Singh et al. (1976), Altshuller (1976), and Galbally (1976). Secondary sources of CCl_4 exist, but their quantitative contribution to the atmospheric budget of CCl_4 cannot be now determined. No natural sources of CCl_4 are known.

The increase in CCl_4 in the atmosphere over the last few years has been small. Figure 17 shows the average growth rate suggested by our data. The growth rate of 2.3 ppt/year (≈2% per year) is in good agreement with the growth rate projected by Singh et al. (1976) from emissions data alone.

It was also found that CCl_4 levels in the urban samples collected in Lisbon were about 180 ppt, about 50% higher than the background level. This observation is consistent with our earlier finding that CCl_4 levels are 20 to 50% higher in urban areas (Singh et al., 1977c).

Methyl Chloroform

CH_3CCl_3 has been found in the atmosphere for several years, but only recently has interest in its fate been shown. This interest resulted from two observations first reported by Singh (1977a, 1977b), who found that the atmospheric burden of CH_3CCl_3 was consistent with an 8-year residence time, contrary to all previous estimates that placed its residence time between 1 and 2 years. A longer residence time meant that CH_3CCl_3 could be a potential depleter of stratospheric ozone and that the average hydroxyl radical (HO) abundance in the troposphere was lower than the earlier estimates by a factor of 5 to 10. Much of the analysis, however, was based on point measurements. Therefore a continuous data base showing the latitudinal variation of CH_3CCl_3 was needed.

Figure 18 shows the global distribution of CH_3CCl_3 and a polynomial fit to it. Note that CH_3CCl_3 shows a latitudinal distribution

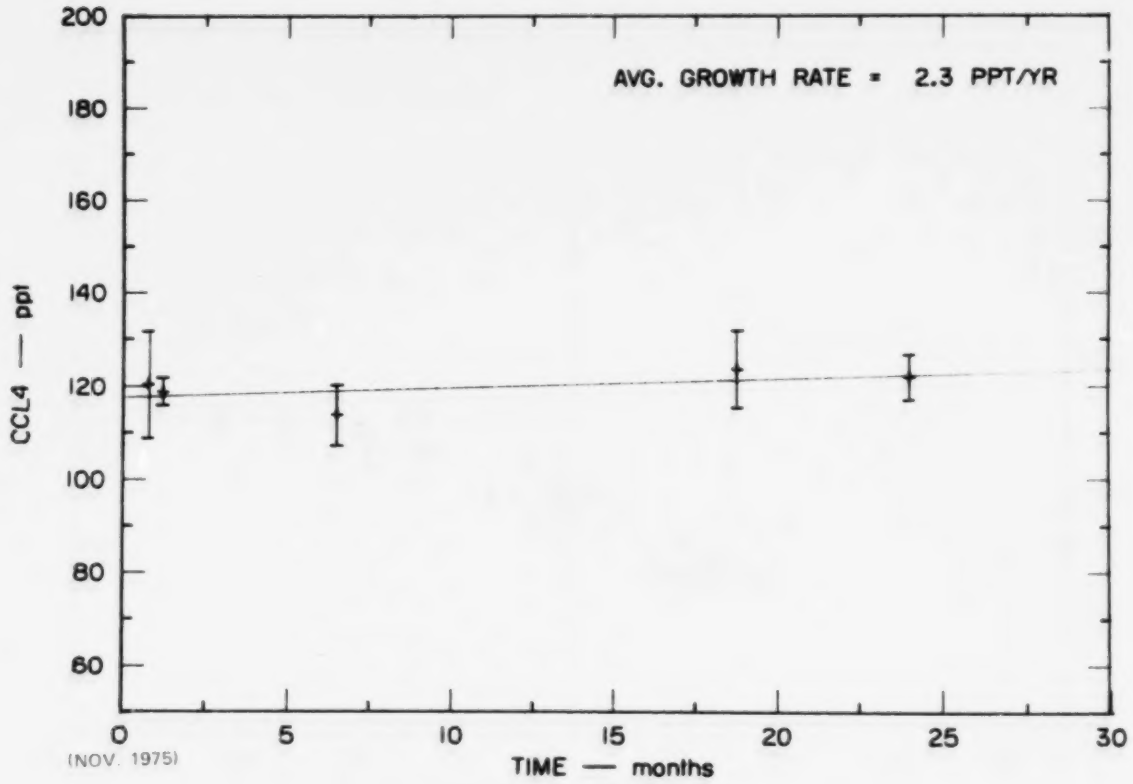

FIGURE 17 GROWTH OF CCl_4 WITH TIME

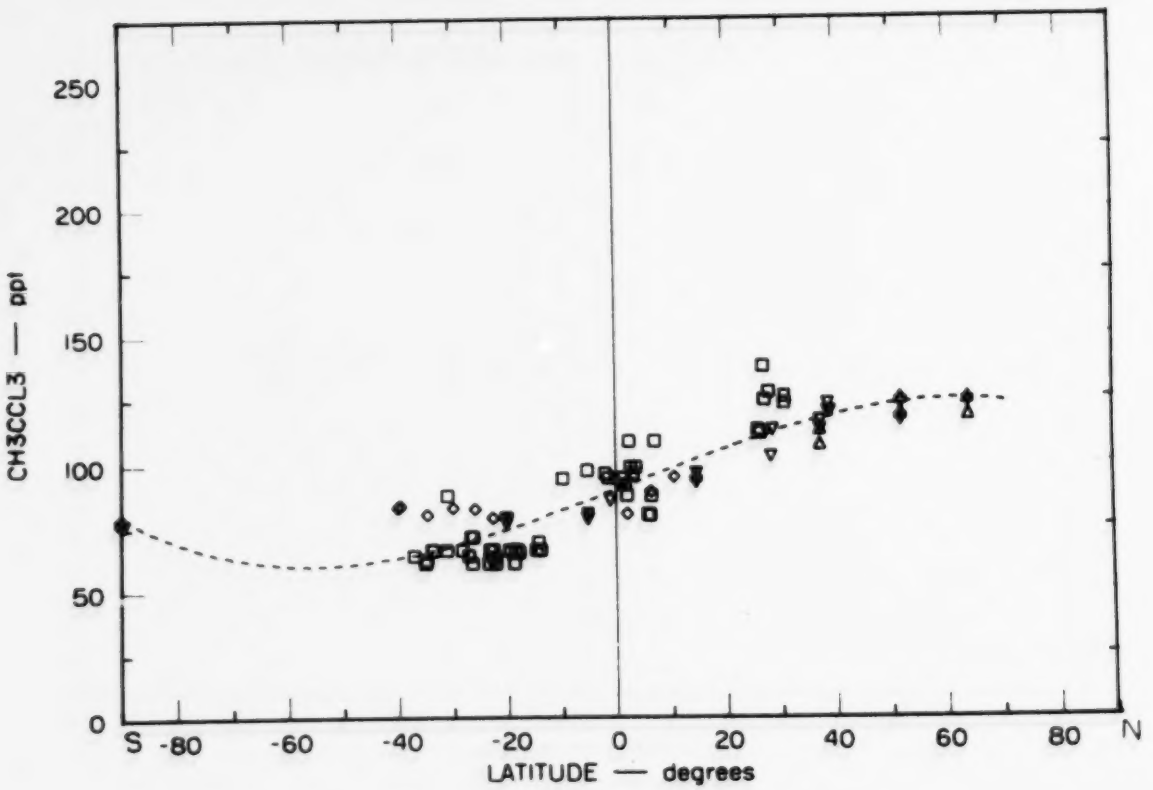

FIGURE 18 GLOBAL DISTRIBUTION OF CH_3CCl_3

quite different from that of the fluorocarbons. Up to about 30°N, the N.H. seems to be well mixed with CH_3CCl_3, with an average concentration of about 120 ppt. A fairly sharp decline seems to occur between 20°N and 20°S; the levels of CH_3CCl_3 seem to level off to about 70 ppt. This decline cannot be attributed to normal mixing processes, since fluorocarbons do not show such a rapid decline. A more plausible explanation of such a phenomenon would be that the HO radical is more abundant around the equator because of the intense sunlight and higher water vapor concentration in this region. Two-dimensional models, however, would be required to adequately model CH_3CCl_3 distribution.

The average, uniformly mixed CH_3CCl_3 concentrations of about 113 ppt in the N.H. and 75 ppt in the S.H. best describe the burden of CH_3CCl_3 in each hemisphere. When used in a two-box model (Singh, 1977b), this hemispheric distribution would indicate an HO concentration that is higher in the southern hemisphere than in the N.H. More detailed calculations will be presented later.

Figure 19 shows that the average growth rate of CH_3CCl_3 at about 40°N has been 15.5 ppt/year ($\approx$17% per year). Emissions data for CH_3CCl_3 between 1976 and 1978 are not available, but an extrapolation of emissions data provided by Dow Chemical Company (Singh, 1977b), suggests that an increase of about 15 to 20%/year can be expected.

The urban concentration of CH_3CCl_3 in Lisbon was 250 ppt, about twice the background concentration.

Methyl Chloride

CH_3Cl has been measured at point sources in the N.H. by a number of researchers, but to the best of our knowledge, S.H. data have never before been reported. Figure 20 shows the latitudinal variation of CH_3Cl that we found. The following results were obtained:

Average CH_3Cl concentration in the N.H. = 611 ± 83.7 ppt
Average CH_3Cl concentration in the S.H. = 615 ± 103.0 ppt
Average global CH_3Cl concentration = 613 ppt.

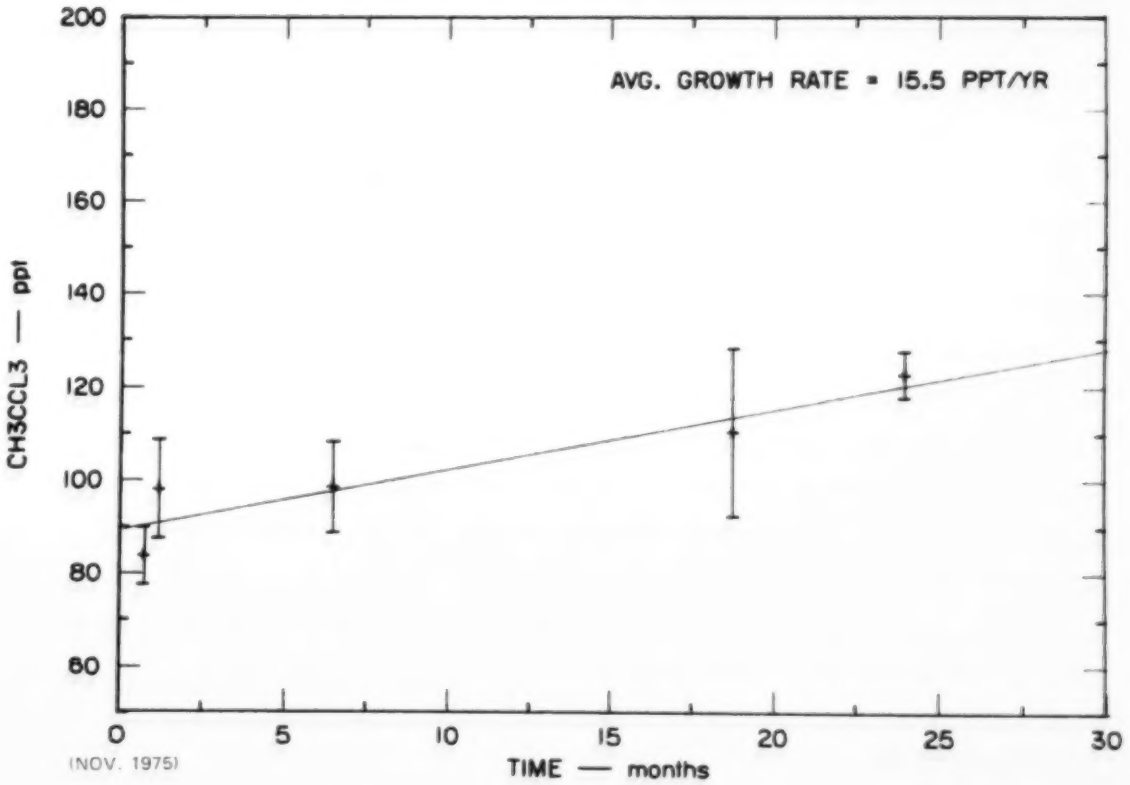

FIGURE 19 GROWTH OF CH_3CCl_3 WITH TIME

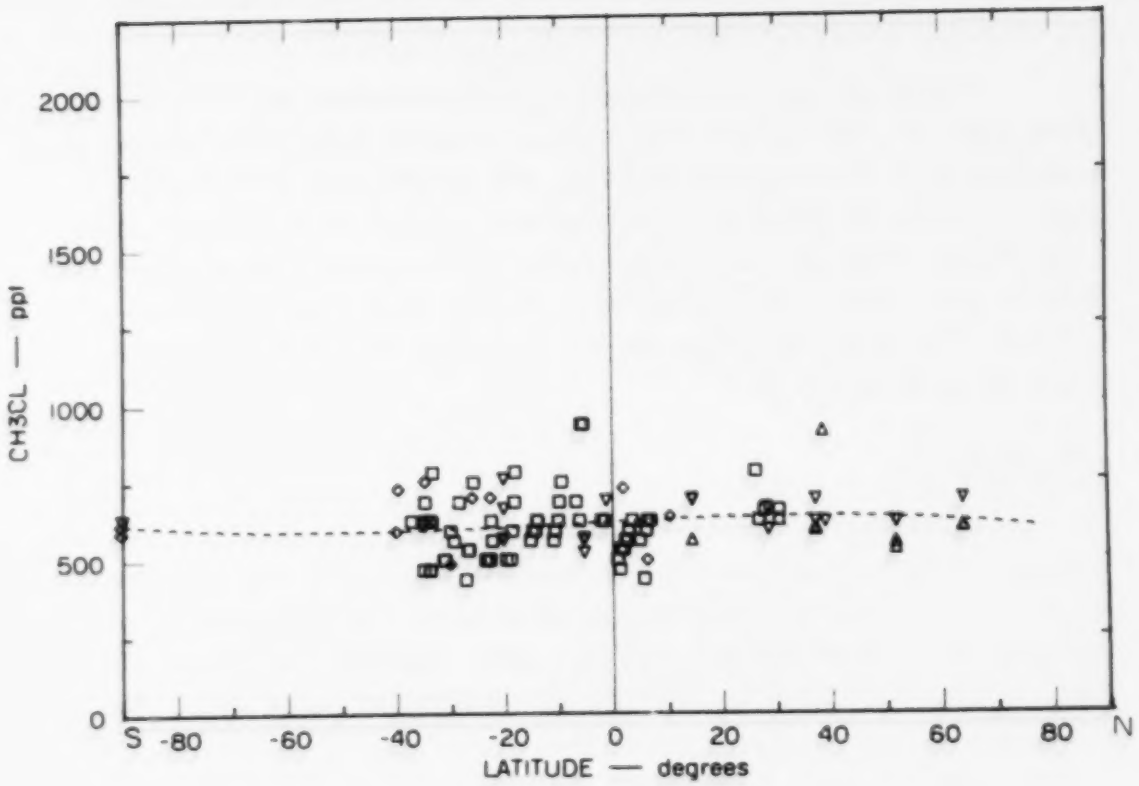

FIGURE 20 GLOBAL DISTRIBUTION OF CH_3Cl

The global distribution of CH_3Cl is essentially uniform, with marginally higher concentrations in the S.H. The 35% larger ocean area available in the S.H. may be a natural source of CH_3Cl. The higher HO levels in the S.H. (Singh, 1977b) may also provide an additional sink for CH_3Cl. The larger reservoir of CH_3Cl, coupled with a lifetime we estimate as 3 years, supports the contention that a significant natural source of CH_3Cl exists. We show in Section VI-B that the ocean may be the single most important source of atmospheric CH_3Cl.

The urban samples collected in Lisbon contained CH_3Cl levels of nearly 2200 ppt. Our earlier studies in Los Angeles (Riverside) showed an average CH_3Cl concentration of 1500 ± 700 ppt (maximum of 3800 ppt), about 2.5 times the background levels measured (Singh, et al., 1977c). Thus a significant urban source of CH_3Cl exists. Since primary emissions of CH_3Cl do not appear to be significant, secondary CH_3Cl sources must be inferred. The possibility that automobile exhaust may be such a source should be investigated.

Methyl Iodide

While CH_3I was present most of the time, its quantitation was difficult because an unknown chemical species or artifact tended to mask the CH_3I peak. Thus CH_3I measurements could be made only when this artifact was resolved from the true CH_3I peak. Therefore the amount of data was limited. Figure 21 shows the global distribution of CH_3I. The following data were obtained:

Average CH_3I concentration in the N.H. = 2.1 ± 1.0 ppt
Average CH_3I concentration in the S.H. = 2.3 ± 1.2 ppt
Average global CH_3I concentration = 2.2 ppt

CH_3I surface levels in the S.H. are somewhat higher than they are in the N.H., with a global average of about 2 ppt. Because of the extremely short lifetime of CH_3I ($\tau < 5$ days), large vertical variability should be expected. Therefore, the surface CH_3I levels cannot be used to obtain an estimate of iodine global burden. The distribution of CH_3I also suggests an oceanic source of CH_3I.

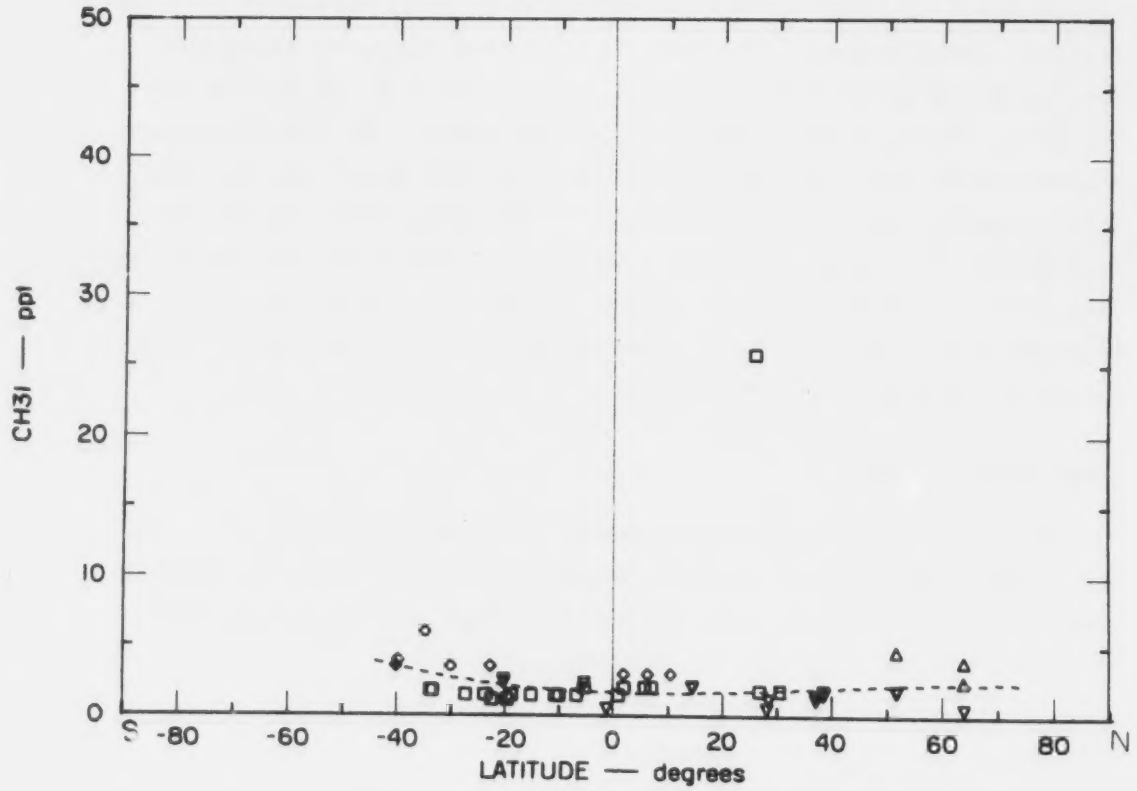

FIGURE 21 GLOBAL DISTRIBUTION OF CH_3I

Chloroform, Methylene Chloride, Trichloroethylene, and Tetrachloroethylene

In-situ analysis requiring cryogenic preconcentration of samples could not be performed on Trip 2 because of turbulent conditions on this trip. Therefore, all the data for these species were obtained via analysis of air samples collected in SS and glass vessels. A good deal of contamination of these species was indicated by their very high and often variable concentrations. The best data obtained suggested background concentrations in the N.H. of 14 ± 7, 44 ± 14, 16 ± 8, and 40 ± 12 ppt for $CHCl_3$, CH_2Cl_2, C_2HCl_3, and C_2Cl_4, respectively. The S.H. background concentrations were very low: ≤ 3, 20 ± 4, <3, and 12 ± 3 ppt for $CHCl_3$, CH_2Cl_2, C_2HCl_3, and C_2Cl_4, respectively. The $CHCl_3$ levels in the S.H. were between 2 to 3 ppt. It must, however, be emphasized that these averages are based on only 5 to 10 samples for each hemisphere that were adjudged clean. They do not adequately take the intrahemispheric variabilities and gradients into account.

LIGHT HYDROCARBONS

Analysis was conducted for a number of light hydrocarbons. Due to the limited number of air samples available and other practical reasons, quantitation was possible only for methane (CH_4), ethane (C_2H_6), and ethylene (C_2H_4).

Methane

Figure 22 shows the global distribution of CH_4. It is clear that CH_4, like most other long-lived species, is practically uniformly distributed. The following data were obtained:

Average CH_4 concentration in the N.H. = 1430 ± 64.7 ppb
Average CH_4 concentration in the S.H. = 1390 ± 51.4 ppb
Average global CH_4 concentration = 1410 ppb

Thus the S.H. CH_4 average concentration is about 3% lower than the N.H. average concentration. This, however, is within the variability of about 5% (σ) associated with the average. Even though large anthropogenic sources

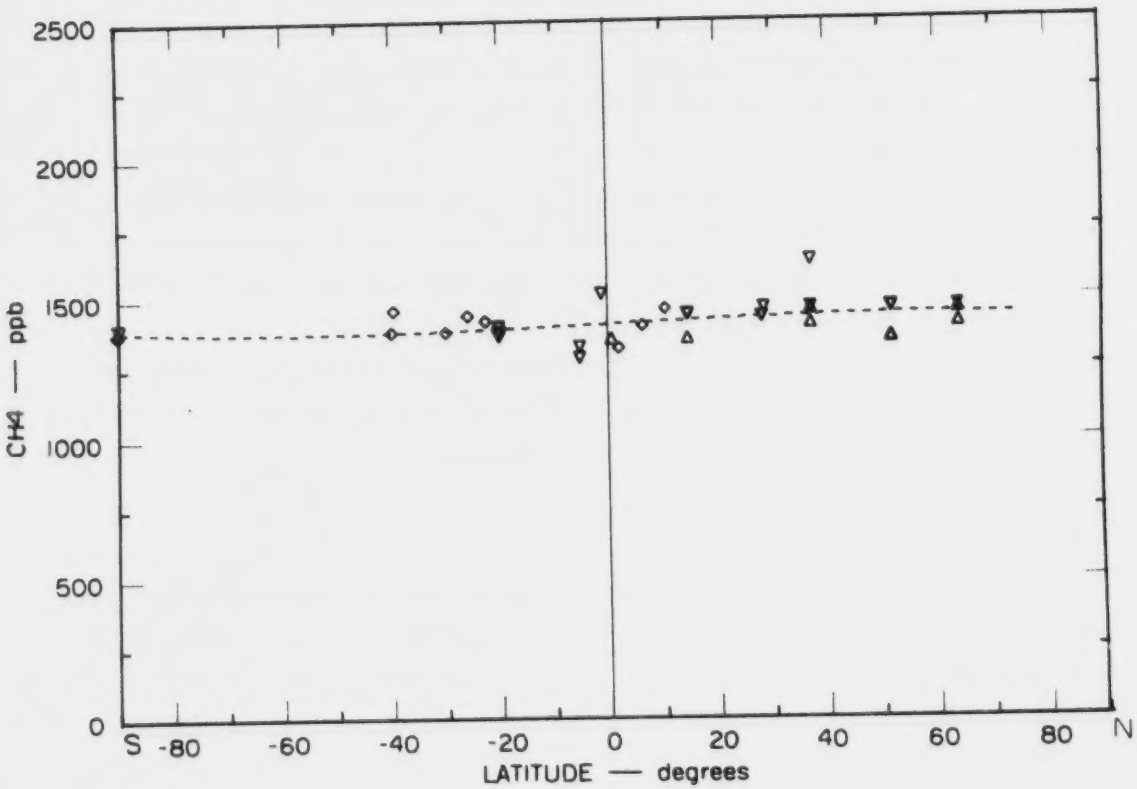

FIGURE 22 GLOBAL DISTRIBUTION OF CH_4

of CH_4 exist in the N.H., CH_4 is largely of natural origin with a very high background concentration and a long tropospheric lifetime. The very long lifetime of CH_4, when taken with the interhemispheric exchange rate, allows for a near-uniform distribution of CH_4 around the globe.

Ethane

C_2H_6 was also ubiquitous in the global atmosphere. The global distribution of C_2H_6 was dissimilar to that of CH_4, probably because C_2H_6 has a much shorter tropospheric lifetime than CH_4 does. Figure 23 shows the nonlinear C_2H_6 distribution in the N.H. At least in the S.H., the concentration of C_2H_6 is relatively uniform, averaging about 0.5 ppb. In the N.H., however, the concentration approaches 2 ppb at mid-northern latitudes but drops off to nearly 1 ppb near the equator. The weighted average concentration of C_2H_6 that represents its burden in the N.H. is calculated to be 1.1 ppb. Thus a very large gradient of C_2H_6 between the N.H. and S.H. exists. The latitudinal profile of C_2H_6 suggests that there are significant sources in the northern hemisphere.

Ethylene and Acetylene

C_2H_4 distribution is shown in Figure 24. We emphazine that some samples were apparently contaminated and unusually variable. The average C_2H_4 concentrations in the N.H. and S.H., for example, were 1.4 ± 1.1 ppb and 1.0 ± 0.6 ppb, respectively. The air samples were probably inadvertently contaminated during sampling. More recently, in-situ analysis in the N.H. suggests that C_2H_4 background concentrations at ground level are less than 0.3 ppb. The problem of sample contamination has also been observed by others (Cronn, D.R., WSU, private communication), but has yet to be adequately resolved. C_2H_4 concentration near the surface may also be highly variable and not representative of the tropospheric background.

Acetylene concentration was found to be below the limit of our measurement sensitivity in both the N.H. and the S.H. (<200 ppt). Limited air sample availability did not allow further improvement in this sensitivity, which would have required sample sizes of 1.5 liters or more.

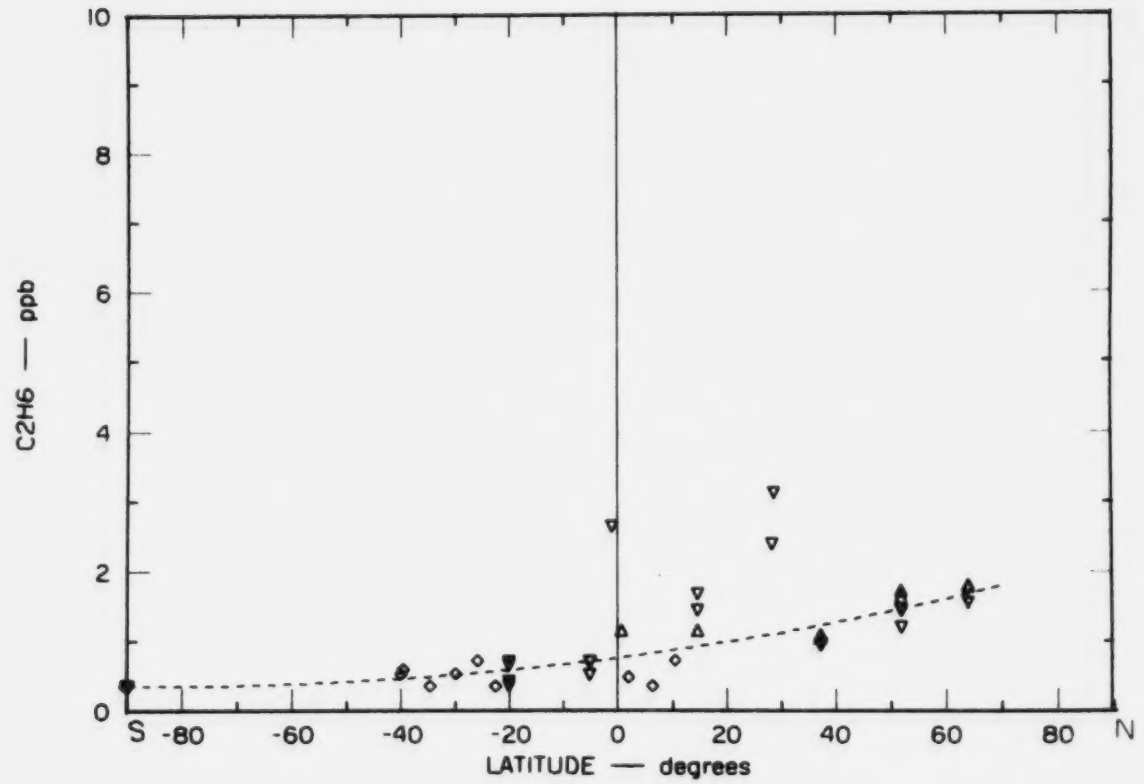

FIGURE 23 GLOBAL DISTRIBUTION OF C_2H_6

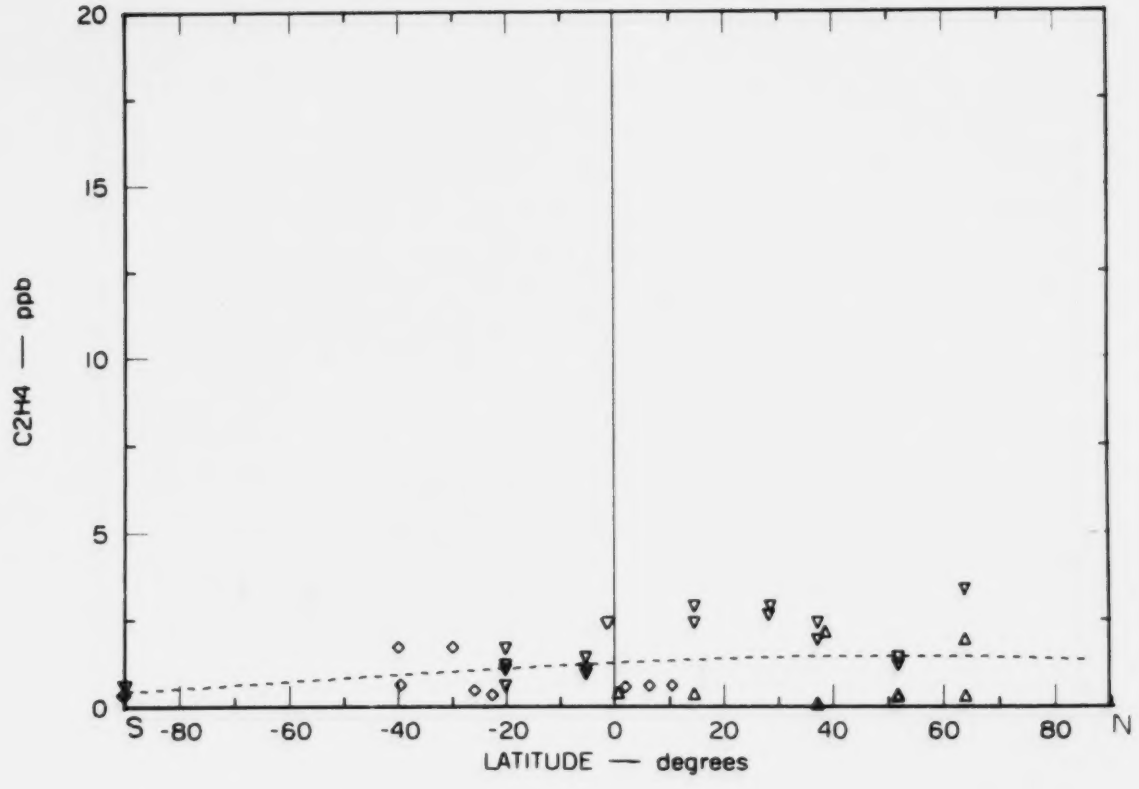

FIGURE 24 GLOBAL DISTRIBUTION OF C_2H_4

PACIFIC SEAWATER MEASUREMENTS--DISTRIBUTION AND FLUX

NITROUS OXIDE

Seawater from the Pacific ocean from 45°N to 39°S was analyzed during Trip 2. On eight occasions, paired water samples were collected from depths of 0 to 300 m at 50-m intervals. The water temperature was recorded at the depth at which a paired water sample was collected. The data from the paired samples were averaged. On two of these occasions only one set of samples could be analyzed because bad weather made further operations impossible. Surface water samples, however, were always collected in duplicate and the results averaged. Surface water samples from 16 different locations were analyzed for N_2O.

As soon as the water sample was collected, 25 ml of the water sample were equilibrated with an equal volume of nitrogen. N_2O was then analyzed in the gas phase, the corresponding water concentration was determined from solubility data, and the amount of N_2O in air and in water were added to obtain the concentration of N_2O in the original water sample. Either ultra-pure air or nitrogen could be used as the inert gas with no perceptible difference in the calculated N_2O concentration. Table 7 shows the

Table 7

N_2O SOLUBILITY IN SEAWATER

Temperature (°C)	0	5	10	15	20	25,	30
Solubility (S)* of N_2O in seawater	1.04	0.89	0.75	0.63	0.53	0.44	0.38

$$^{*}S = \frac{\text{Concentration at the ocean-air interface}}{\text{Atmospheric concentration at STP}}.$$

solubility data used in our calculations--a corrected version of data originally published by Junge et al. (1971), which derived them from experiments conducted by Markham and Kobe (1941). The correct data were provided by J. Hahn (Max Planck Institute, Mainz, West Germany).

Table 8 shows the measured water temperature and N_2O concentration at depths of 0, 50, 100, 150, 200, 250, and 300 m, and the calculated percentage N_2O saturation in seawater. In every instance, a supersaturation of N_2O was observed. Figure 25 shows plots of N_2O concentration in seawater, N_2O saturation, and water temperature as they vary with depth. Clear evidence of N_2O synthesis below the mixed layer is visible. The N_2O production below the mixed layer showed maximum near the equatorial region, and only marginal supersaturation was observed at southern midlatitudes. Saturation is most significant near 11°N. It is least evident at 39°S, perhaps because the reduced biological activity results in conditions not greatly favorable to denitrification. Typically, however, between 45°N and 40°S in the Pacific, N_2O concentration below the mixed layer can be 1 to 7 times the surface concentration. The North Pacific is low in oxygen and therefore suited for N_2O formation via bacterial denitrification processes, but in the Western South Pacific the oxygen content is an order of magnitude higher than it is in the North Pacific [4 to 5 ml $(O_2)/l$]. We suggest that N_2O can be synthesized in colder waters where the oxygen content is considerably higher than 0.3 ml $(O_2)/l$. All these observations suggest one of two major possibilities. Either nitrification processes that are efficient under relatively high O_2 abundance play a more significant role in N_2O production than is now believed, or denitrification processes are currently poorly understood, and denitrification can proceed under conditions significantly different from anoxic. The amount of N_2O synthesis in the southern midlatitudes does seem to be small when compared to that in the north midlatitude region of the Pacific.

The surface water was always supersaturated with N_2O, and these waters largely determine the flux of N_2O into the atmosphere. The surface N_2O concentrations and saturation levels are shown in Table 9. Figure 26 shows a plot of the N_2O concentration in surface water, N_2O saturation in surface water, average N_2O saturation in water between 200 and 300 m

Table 8

N_2O CONCENTRATION IN THE PACIFIC OCEAN

Depth (m)	Date 10-29-76 Lat 45°35'N Long 125°55'W			Date 10-28-76 Lat 41°35'N Long 125°55'W			Date 11-25-77 Lat 19°02'N Long 137°48'W			Date 11-27-77 Lat 11°52'S Long 142°05'W			Date 11-30-77 Lat 01°26'S Long 150°10'W			Date 12-6-77 Lat 25°40'W Long 167°33'W			Date 12-8-77 Lat 33°40'S Long 170°50'W			Date 12-11-77 Lat 39°05'S Long 179°13'W		
	Water Temp (°C)	N_2O (μg/l)	% Sat	Water Temp (°C)	N_2O (μg/l)	% Sat	Water Temp (°C)	N_2O (μg/l)	% Sat	Water Temp (°C)	N_2O (μg/l)	% Sat	Water Temp (°C)	N_2O (μg/l)	% Sat	Water Temp (°C)	N_2O (μg/l)	% Sat	Water Temp (°C)	N_2O (μg/l)	% Sat	Water Temp (°C)	N_2O (μg/l)	% Sat
0	13.5	0.46	115	14.2	0.46	120	24.3	0.36	133	25.4	0.41	152	27.6	0.48	190	23.2	0.36	124	18.5	0.40	119	16.9	0.42	118
50	12.2	0.56	136	13.2	0.58	145	24.0	0.78	289	17.4	0.83	237	27.5	0.34	135	21.8	0.40	133	14.6	0.44	144	16.8	0.47	132
100	10.5	0.73	166	12.0	0.71	169	24.0	0.58	215	12.2	2.48	605	27.5	0.39	154	19.4	0.40	123	13.5	0.50	125	14.7	0.43	113
150	9.6	0.95	213	10.7	0.96	218	20.6	0.42	133	11.8	2.83	690	25.8	0.40	149	18.5	0.48	143	12.7	0.58	141	13.7	0.47	119
200	9.0	1.27	270	10.0	1.08	237	19.2	0.40	121	11.1	2.09	486	19.0	0.93	282	17.7	0.42	120	12.2	0.59	144	13.4	0.47	118
250	8.6	1.37	291	9.5	1.16	252	17.3	0.51	146	10.6	2.10	477	13.6	2.08	527	16.3	0.46	127	11.7	0.58	141	13.1	0.45	113
300	8.2	1.42	296	9.2	1.18	257	12.4	0.93	227	10.2	2.31	519	13.4	1.35	342	15.2	0.49	130	10.7	0.65	148	13.0	0.41	103

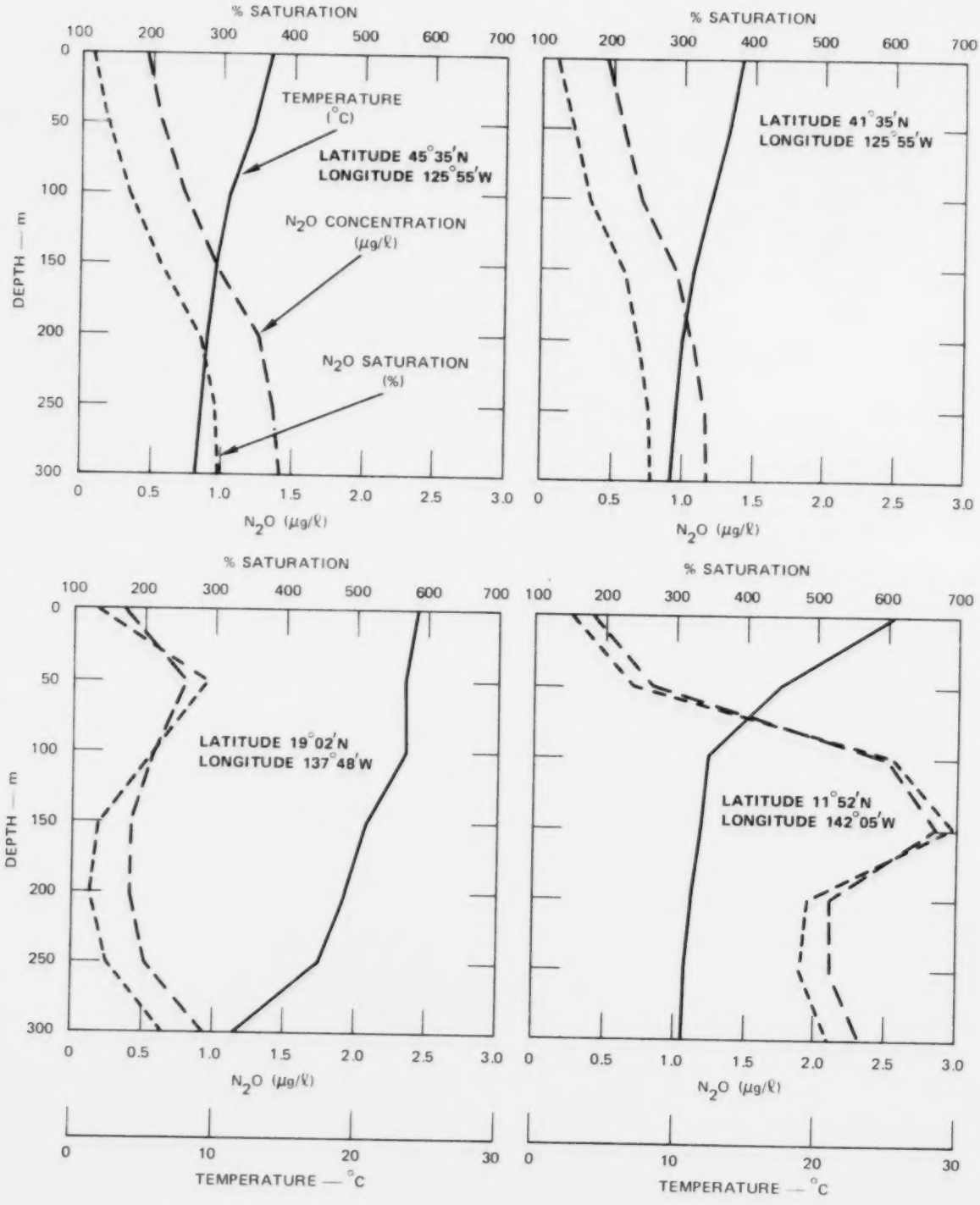

FIGURE 25 N_2O VARIATION WITH DEPTH IN THE PACIFIC OCEAN

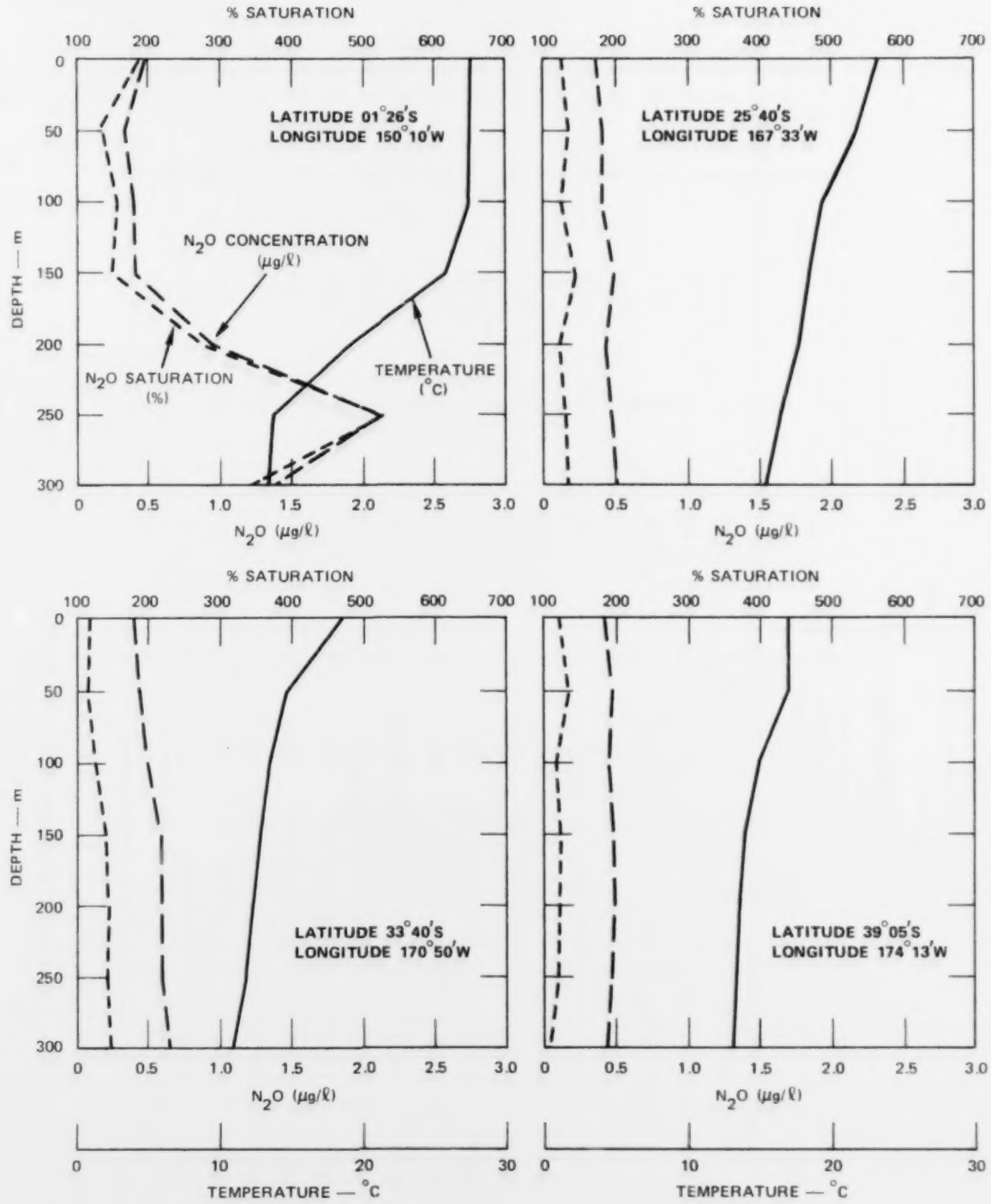

FIGURE 25 (Concluded)

Table 9

N_2O CONCENTRATION IN PACIFIC SURFACE WATER*

Date	Lat	Long	Surface Water Temp (C°)	N_2O Concentration (μg/l)	N_2O Saturation	Flux† x 10^{-12} (g/cm^2 s)
10-29-76	45°35'N	125°55'W	13.5	0.46	115	0.173
10-28-76	41°35'N	125°35'W	14.2	0.46	120	0.224
11-25-77	19°02'N	137°48'W	24.3	0.36	133	0.347
11-26-77	15°43'N	140°05'W	25.5	0.35	130	0.323
11-27-77	11°52'N	142°05'W	25.4	0.41	152	0.561
11-28-77	06°35'N	145°14'W	28.4	0.31	124	0.258
11-29-77	02°40'N	147°43'W	26.5	0.37	141	0.438
11-30-77	01°26'S	150°10'W	27.6	0.48	190	0.955
12-01-77	06°07'S	153°13'W	28.1	0.31	125	0.264
12-02-77	09°07'S	155°35'W	28.8	0.31	124	0.261
12-04-77	18°24'S	161°42'W	26.7	0.46	175	0.808
12-05-77	22°38'S	164°26'W	24.8	0.34	128	0.291
12-06-77	25°40'S	167°33'W	23.2	0.36	124	0.261
12-07-77	30°14'S	171°18'W	21.5	0.35	115	0.164
12-08-77	33°40'S	170°50'W	18.5	0.40	119	0.211
12-11-77	39°05'S	179°13'W	16.9	0.42	118	0.204
Average				0.38	133	0.359

*Water from 0 to 2 meters.

†Flux calculation assumes a stagnant film thickness of 60 μm.

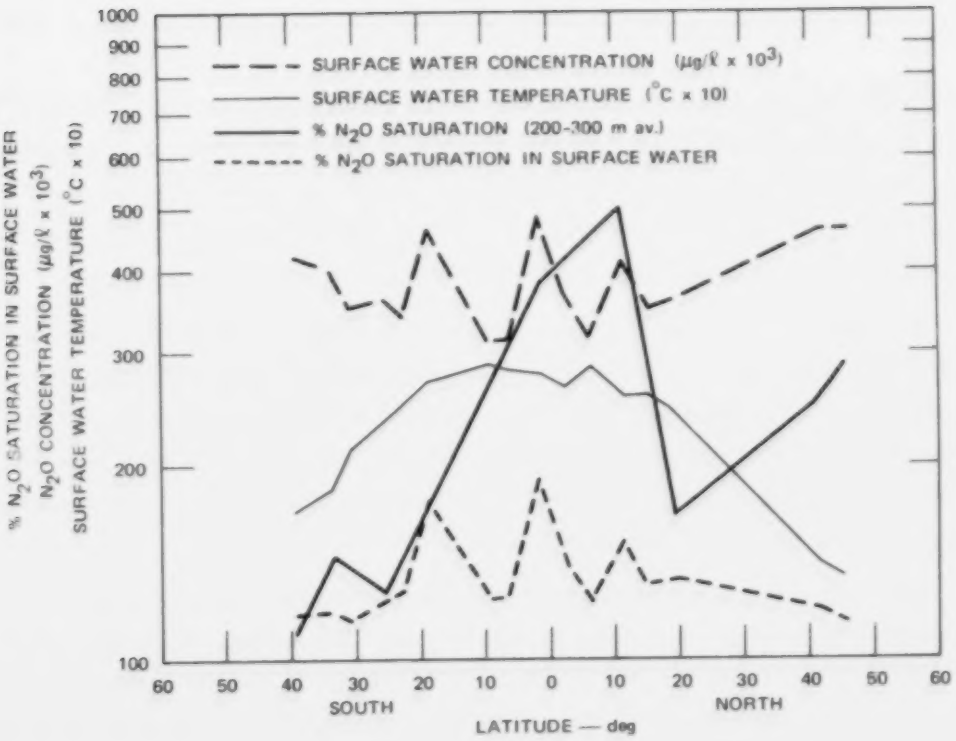

FIGURE 26 N_2O SUPERSATURATION IN THE PACIFIC OCEAN (46°N-40°S)

in depth, and the surface water temperature as they vary with latitude. The average N_2O between 200 and 300 m shows a decline from mid-northern to low-northern latitudes, a maximum near the equator, and a rapid decline in the southern hemisphere.

From the data in Table 9, it is possible to calculate the flux, F, of N_2O into the atmosphere by using a simple film diffusion model:

$$F = \frac{D(T)}{Z} (C^w - C^w_{eq}) \qquad (4)$$

where D(T) is the film diffusion coefficient for N_2O in water and is a function of temperature; Z is the stagnant film depth (Broecker and Peng, 1974) which has been measured to be 60 ± 30 μm (μm = 10^{-6} m) for the world ocean; C^w is the concentration of N_2O in water; and C^w_{eq} is the N_2O concentration in equilibrium with the atmospheric abundance of N_2O.

For our calculations we have selected Z = 60 μm and used the solubility data presented in Table 7. The variation of D(T) with temperature was obtained from Broecker and Peng (1974). Our choice of Z is the one recommended by Hahn and Junge (1977), but the actual value of Z may be higher than 60 μm for a biologically active gas such as N_2O. The mean N_2O concentration in the atmosphere was taken to be 311 ppb.

The flux estimates calculated for each surface site are shown in Table 9. The average N_2O flux is 0.359×10^{-12} g/cm^2 s. The N_2O saturation of 133% we found in the Pacific (45°N to 40°S) can be compared with the 123% saturation found by Hahn (1974) in the Atlantic between 38°N and 50°N and the 132% saturation found by Rasmussen et al. (1976) in the eastern tropical Pacific (31°N to 11°S). Rasmussen's figure, however, is probably too low, since he used the solubility data published by Junge et al. (1971), which were found to be in error. In 1969 Hahn (1974) measured an average saturation of 180% between 0 and 60°N, but three of the seven available data points were unusually high. Preliminary data from the Pacific ocean were provided by Craig and Gordon (1963), but the measurement techniques were insensitive. Our current data remedies this deficiency significantly. This is especially so, since the preliminary data of Craig and Gordon have been extended by some recent investigators (McElroy et al., 1976) to suggest that oceans are a net sink for N_2O.

A comparison of our data with those of Hahn (1974) and Rasmussen et al. (1976) suggests that our measured average N_2O saturation of 133% in the Pacific is representative of that of global waters between 45°N and 45°S. About 74% of the total water surface is between these latitudes. In the rest of the ocean, the surface supersaturation of N_2O is about half this average; from the data provided by Hahn (1974) it is reasonable to assume that this saturation is 115%.

Assuming an average flux of 0.359×10^{-12} g/cm^2 s for the world ocean waters, we calculate a net flux of 38.5×10^{12} g/year, or 38.5 million tons/year for an ocean area of 3.61×10^{18} cm^2. However, using 133% saturation for the 74% of the seawater area between 45°N and 45°S and 115% for the remaining water surface, the average global N_2O flux is 32.4 million tons/year. This estimate of N_2O flux from ocean waters is less than half the best estimate of 70 million tons/year by Hahn and Junge (1977) and about a quarter of Hahn's (1974) original estimate. Fresh water surfaces (2×10^{16} cm^2) can provide an N_2O source of 1 to 4 million tons, and combustion sources are likely to be less than 4 million tons (Hahn and Junge , 1977). Our best estimate of N_2O flux from oceanic and fresh water sources is about 35 million tons/year. The atmospheric burden of N_2O is about 2.34×10^3 million tons/year, which corresponds to an average N_2O level of 311 ppb in air. Using this atmospheric abundance and a flux of 35 million tons/year, we calculate an N_2O residence time of 67 years. This is surprisingly close to the upper limit of a 60-year residence time estimated from the atmospheric variability of N_2O. The stratospheric sink has been estimated to cause a turnover rate of about 120 years. Since our data indicate that the N_2O background is at a steady state, an unknown sink with a residence time of about 150 years can be inferred. The possibility that this sink is the soil is suggested. Soil as a net sink for N_2O has also been supported by some recent experiments of Blackmer and Bremner (1976), who find that although N_2O is synthesized in soil, it is reconverted to N_2 during diffusion upward.

The saturation of the ocean waters supports the hypothesis that the ocean is a source of N_2O. McElroy et al. (1976), based on a different interpretation of Hahn's (1974) and Craig and Gordon's (1963) data,

suggested that the soil is the major source of N_2O and that the ocean is a net sink. This allows one to argue that N_2O abundance would increase with increased use of fertilizer on soil, but the evidence does not sup- this contention. As long as the ocean is a major source of N_2O, any effect on the N_2O abundance from increased use of fertilizer is likely to be very marginal. In fact the possibility that some of man's activities may actually reduce N_2O (Ellsaesser, 1977) can also not be ruled out.

B. Halocarbons

A preliminary attempt was made to measure halocarbons in seawater, using the technique used for N_2O. Solubility data for F11 and F12 were obtained from Junge (1976), and for other chlorinated species from Dilling (1977). The variations of CCl_4 and CH_3Cl solubility with temperature were not available but were assumed to be similar to F11 variation. It was possible to obtain quantitative data for F12, F11, CCl_4, and CH_3Cl. The data on CH_3CCl_3 were unusually high and were discarded as contaminated. Table 10 shows the variation of F12 in seawater. The average surface concentration was 0.28 ng/l. Typically, the F12 concentration was highest at the surface and declined with depth. Occasionally, however, an increase in concentration was observed with depth. We suspect that this reflects contamination of water samples.

Table 11 shows the surface concentration of F12, F11, CCl_4, CH_3Cl, and $CHCl_3$. The average concentrations of individual species at 0 and 300 m are given in Table 12. The average surface water concentrations of of F12, F11, CCl_4, CH_3Cl, and $CHCl_3$ are 0.28, 0.13, 0.40, 26.8, and <0.05 ng/l, respectively. The corresponding average concentrations at 300m are shown in Table 12. It can be seen from Table 11 that the concentration of CH_3Cl shows large variation. Typically the values seemed to be higher near the equator. It also appears that CH_3Cl is largely synthesized in the upper layers of the ocean waters, but the data base is too limited to draw any firm conclusions. $CHCl_3$ could not be identified in seawater and we must conclude that its concentration in seawater is less than 0.05 ng/l. Since we know the surface water concentration of halocarbons, we can determine

Table 10

F12 CONCENTRATIONS IN THE PACIFIC OCEAN

Depth (m)	Date 11-25-77 Lat 19°02'N Long 137°46'W		Date 11-27-77 Lat 11°52'N Long 142°25'W		Date 11-30-77 Lat 01°26'S Long 150°10'W		Date 12-6-77 Lat 25°40'S Long 167°33'W		Date 12-8-77 Lat 33°40'S Long 173°50'W		Date 12-11-77 Lat 39°05'S Long 179°13'W	
	ng/l	Temp (°C)	ng/l	Temp (°C)	ng/l	Temp (°C)	ng/l	Temp (°C)	ng/l	Temp (°C)	ng/l	Temp (°C)
0	0.40	24.3	0.32	25.4	0.35	27.6	0.25	23.2	0.19	18.5	0.53	16.9
50	0.20	24.0	0.23	17.4	0.25	27.5	0.20	21.8	0.20	14.6	0.18	16.8
100	0.32	24.0	0.23	12.2	0.28	27.5	0.20	19.4	0.22	13.5	0.10	14.7
150	0.15	20.6	0.56	11.8	0.33	25.8	0.25	18.5	0.25	12.7	0.09	13.7
200	0.15	19.2	0.42	11.1	0.31	19.0	0.25	17.7	0.24	12.2	0.09	13.4
250	0.22	17.3	0.24	10.6	0.24	13.6	0.45	16.3	0.27	11.7	0.09	13.1
300	0.20	12.4	0.07	10.2	0.24	13.4	0.45	15.2	--	10.7	0.09	13.0

Table 11

CONCENTRATIONS OF HALOCARBONS IN SURFACE SEAWATER
(0-2 m)

Date	Lat	Long	Water Temp (°C)	Concentration (ng/l)				
				F12	F11	CCl_4	CH_3Cl	$CHCl_3$
11-25-77	19°02'N	137°48'W	24.3	0.40	--	--	--	--
11-26-77	15°43'N	140°05'W	25.5	0.32	--	--	--	--
11-27-77	11°52'N	142°25'W	25.4	0.32	--	--	--	--
11-28-77	06°35'N	145°14'W	28.4	0.47	--	--	--	--
11-29-77	02°35'N	145°14'W	26.5	0.07	--	--	--	--
11-30-77	01°26'S	150°10'W	27.6	0.35	--	--	--	--
12-01-77	06°07'S	153°13'W	28.1	0.14	--	--	--	--
12-02-77	09°07'S	155°75'W	28.8	0.07	0.15	0.41	34.5	<0.05
12-04-77	18°24'S	161°42'W	26.7	0.14	0.24	0.45	85.8	<0.05
12-06-77	25°40'S	167°33'W	23.2	0.25	0.07	0.35	21.2	<0.05
12-07-77	30°14'S	171°18'W	21.5	0.40	0.10	0.38	1.4	<0.05
12-08-77	33°40'S	173°50'W	18.5	0.19	0.10	0.40	12.5	<0.05
12-11-77	39°05'S	179°13'W	16.9	0.53	0.12	0.40	5.3	<0.05
Average				0.28 ± 0.15	0.13 ± 0.06	0.40 ± 0.03	26.8 ± 31.2	<0.05

Table 12

AVERAGE CONCENTRATION OF HALOCARBONS IN THE PACIFIC OCEAN

Depth (m)	F12		F11		CCl_4		CH_3Cl		$CHCl_3$	
	Conc (ng/l)	No. of Data Points	Conc (ng/l)	No. of Data Points	Conc (ng/l)	No. of Data Points	Conc (ng/l)	No. of Data Points	Conc (ng/l)	No. of Data Points
0	0.28	13	0.13	6	0.40	6	26.8	6	<0.05	6
300	0.21	5	0.06	2	0.15	2	3.3	2	<0.05	2

the ability of the ocean to act as a source or a sink for halogenated species using the film diffusion model used for N_2O:

$$F = \frac{D(T)}{Z} (C^W - C^W_{eq}) \qquad (5)$$

where F is the flux from the ocean to the air.

Fluorocarbons 12 and 11. Solubility data for F12 and F11 suggest that, if the surface water is in equilibrium with the atmospheric burden, the concentrations of F12 and F11 in water should be about 0.05 and 0.06 ng/l, respectively. These concentrations are lower than the measured average concentrations of 0.28 and 0.13 ng/l, so it appears that the ocean water is supersaturated with F12 and F11. This means that either the solubility data are inaccurate or the water samples were inadvertently contaminated. It is also possible that the ocean surface waters have been contaminated by man-made activities on a global scale. The lowest concentration of F12 and F11 measured, 0.07 ng/l, is about what one would expect if the surface water were saturated with F12 and F11. If the surface water is saturated, the ocean would be a relatively ineffective sink for F12 and F11 but could act as a reservoir that contains less than 0.5% of the atmospheric abundance of F12 and F11 in a steady-state situation.

Carbon Tetrachloride. The average surface water concentration for CCl_4 was 0.40 ng/l, and the average ocean water temperature for these samples was about 23°C. It is thus possible to calculate the flux of CCl_4 into the ocean using Eq. (5) with the following constants:

$$D = 10^{-5} \text{ cm}^2/\text{s}$$
$$Z = 90 \text{ μm}$$
$$S_{CCl_4} = 0.85.$$

A high Z is used because CCl_4 is rapidly absorbed in fatty tissues and may be biologically active. For such species the upper limit of the stagnant film thickness calculated from Radon data, (63 ± 30 μm) is more appropriate. Using Eq. (5) we can calculate a flux:

$$-F_{CCl_4} = 2.8 \times 10^{-16} \text{ g/cm}^2 \text{ s} \qquad (6)$$

If we assume that this flux is typical of all oceans, we can calculate an exchange rate of 3.2×10^{10} g/year. The atmospheric burden of CCl_4 from our measurements is calculated as 3.2×10^{12} g. Thus the ocean should be a sink for CCl_4. The residence time τ_{CCl_4} can be calculated as follows:

$$\tau_{CCl_4} = \frac{3.2 \times 10^{12}}{3.2 \times 10^{10}} = 100 \text{ years.} \qquad (7)$$

Thus our measurements indicate that the ocean can provide a sink for CCl_4 that is about half as effective as the stratospheric sink.

Methyl Chloride. It is obvious from Table 11 that the surface concentration of CH_3Cl in the Pacific is quite variable, with values somewhat higher near the equator. The average surface concentration was 26.8 ng/l. Using an S_{CH_3Cl} of 2.65 (Dilling, 1977) and other parameters defined earlier, we estimate from Eq. (5):

$$F = 2.6 \times 10^{-14} \text{ g/cm}^2 \text{ s} \qquad (8)$$

Extending this to the world ocean body, we calculate an exchange rate of 3.0×10^{12} g/year. From our measurements, the atmospheric burden of CH_3Cl can be calculated to be 5.5×10^{12} g. The turnover time (τ_{CH_3Cl}) from the ocean source is:

$$\tau_{CH_3Cl} = \frac{5.5 \times 10^{12}}{3.0 \times 10^{12}} = 1.8 \text{ years} \quad . \qquad (9)$$

Thus the ocean seems to act as a significant source of CH_3Cl and provides a turnover rate of about two years.

CONCLUSIONS

We conclude that inert halocarbons, such as fluorocarbons 11, 12, 113, and 114 are reasonably well distributed around the globe, with southern hemispheric background concentrations that are only marginally different ($\approx$10%) from the northern hemispheric background concentrations. Most of the known sources exist in the northern hemisphere. This implies an interhemispheric exchange time of about 1 year. Our data also suggest that no significant sinks in the troposphere exist for F11 and F12. The atmospheric lifetimes of F11 and F12 are found to be much higher than those calculated by Jesson et al. (1977). This is because the southern hemispheric concentrations measured by us are significantly higher than those suggested by Lovelock (1973) and used by Jesson et al.

The abundance of HO in the southern hemisphere and near the equator is high compared to HO levels in the northern hemisphere. Atmospheric carbon monoxide, a sink for HO, is invoked as the reason for an asymmetric HO distribution in the two hemispheres.

We found the atmospheric growth of N_2O to be negligible over a 27-month period, and our data suggest a 60-to-70-year residence time of N_2O in the atmosphere. The absence of any increase in N_2O in the atmosphere, when coupled with a long lifetime, suggests that soil is not a significant source of N_2O and may even be a net sink. These observations imply that continued use of fertilizers is unlikely to perturb the N_2O balance for several decades, and thus no significant effect on the stratospheric ozone can be expected. The possibility that our current agricultural practices may actually increase the stratospheric ozone can also not be ruled out.

The oceans are also found to be sinks for atmospheric CCl_4 that are about half as important as the stratospheric sink. A large source of CH_3Cl is found in the Pacific Ocean. Contrary to present belief, we conclude that significant primary or secondary anthropogenic sources of CH_3Cl also exist. The ocean surface water appears to be somewhat supersaturated

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with F11 and F12. The lowest measured values of F11 and F12 would suggest that ocean surface water is in essential equilibrium with their atmospheric burden. These observations suggest that while the ocean may be a small reservoir for F11 and F12, it is an ineffective sink. It is also possible that the anthropogenic contamination of sea surface water has occurred on a global scale. The burden of halocarbons in the globe is growing at a rate that is proportional to the man-made emissions.

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